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Membrane processes in biorefinery applications

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ABSTRACT

The 1st generation of biofuels stemming from sugar cane, rape or corn is commercially established today and holds a considerable market share as a drop-in fuel. However, due to interference with the food chain, the ethical discussion on 'fuel or food' has originated. Therefore, current research focuses on the utilization of lignocellulosic materials as a bio-renewable feedstock. Simultaneously several biomass-based processes were developed over the past decade suggesting scenarios from a classic biofuel plant to a new biorefinery concept which produces for instance polymers which were previous fossil resources based. The growth of bio resource based chemicals, functional monomers as well as fuels leads to an increased demand for new separation processes. This review highlights the role of membrane separations within current and future biofuel and biorefinery scenarios. Membrane processes reviewed are for instance pervaporation for alcohol recovery and ultrafiltration of canola oil, as well as new developments such as the ultrafiltration/nanofiltration of lignin in a solvent-based lignocellulose conversion process or the recovery of amino acids via electrodialysis. The membrane processes are classically categorized as concentration-driven membrane processes, pressure-driven membrane processes, electrical-driven membrane processes and prospective membrane processes. It follows the transition of a classic biofuel production plant to a new sophisticated biorefinery. The review closes with a reflection of membrane-based downstream processes required in a biorefinery transforming cellulose into an itaconic acid.

Contents

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1. Introduction

Recently, biofuels such as biodiesel and bioethanol have been introduced to the world-market as drop-in fuels for regular fuels. Their increasing market share is anticipated to lead to a reduced dependency on fossil-based fuels [1–3]. The success of the so-called 1st generation biofuels — biodiesel (methyl ester) obtained from plant oil and bioethanol obtained from sugar cane or corn — can be explained by its simple production routes. These routes included some membrane-based downstream processes, e.g. the purification of methyl ester via ultrafiltration and subsequent phase separation or the recovery and purification of bioethanol via coupled distillation and pervaporation. Process concepts for biofuel production plants with integrated membrane separation have been reported in various reviews on bioethanol production [4–10]. For example Cardona et al. stated in their review on fuel ethanol production that coupling of pervaporation for the recovery of absolute (anhydrous) ethanol with a previous distillation step allows for cost savings of 12% [5].

The rapid development of 1st generation biofuels led to an increasing competition of food-related biomass for fuel production [11,12]. Therefore, current research focuses on the conversion of lignocellulosic material stemming from wood or grass to biofuel. Processing of this matter is more difficult, due to the strong integration of the lignocellulosic fractions (cellulose, hemicellulose and lignin). Consequently, 2nd generation biorefinery processes which utilize these materials have to comprise more complex conversion routes. An exemplary route would consist of the solvent-based disintegration of the lignocellulose fractions, a subsequent enzymatic hydrolysis of cellulose to glucose and a fermentation of glucose to ethanol. Obviously, the demand for downstream processes increases due to the necessity to recover the solvent or to fractionate the dissolved biomass in fractions such as lignin or amino acids as occurring in grass refining.

Processing of biomass gives the opportunity to make use of the side-products in order to replace fossil oil-based routes beside biofuel production. Fig. 1 visualizes the product line-up which has to be provided by a high efficiency biorefinery. Up to now there are several articles published which discuss biorefinery concepts utilizing lignocellulosic material [14–23]. Especially the fractionation of the crop ingredients is in focus due to the reasons named above [24]. For example lignin, which contributes to 20–30 wt% of wood, may be a potential substitute for conventional plastics due to its high carbon and aromatics content [25]. In order to utilize as many bio-compounds as possible, a comprehensive toolbox of separation processes needs to be at hand. This review focuses on developments of membrane processes for biorefinery applications.

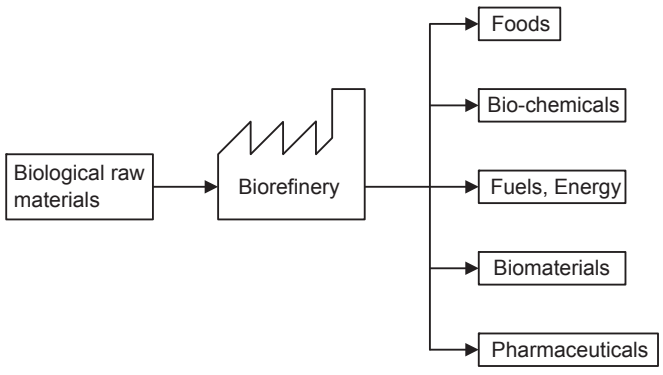

Fig. 1. Visualization of the product line-up which may potentially replace fossil fuel based refineries with biorefining of renewable biomass. Scheme adapted from [13].

For the largest part, the review elucidates the last decade (years 2002–2012) with Fig. 2 showing the development of journal article publications and patent registrations. However, in some important cases older references are reviewed as well. The number of research articles combining the key words of the respective membrane operations (e.g. "ultrafiltration") and "biorefinery" significantly increased, especially over the past 4 years. The evolution of patent publications for membranes in biorefinery is similarly increasing indicating that this topic will be given a high attention in the future.

The review aims to give a comprehensive overview of the relevant membrane processes which are technically established in other areas, but may contribute to efficient biorefinery processes as well. The review does not include gas separation processes which we recently reviewed in [26] for the conversion of biogas into biomethane. Wastewater treatment by means of a membrane bioreactor (MBR) and membrane based water recovery or reuse in a potential biorefinery by means of reverse osmosis (RO) are also excluded from this paper, because they are already established as separate topics in the membrane community and are covered by other comprehensive reviews [27,28]. We start with an overview of pervaporation (PV) and vapor permeation processes which have already been extensively studied in the past and found their way

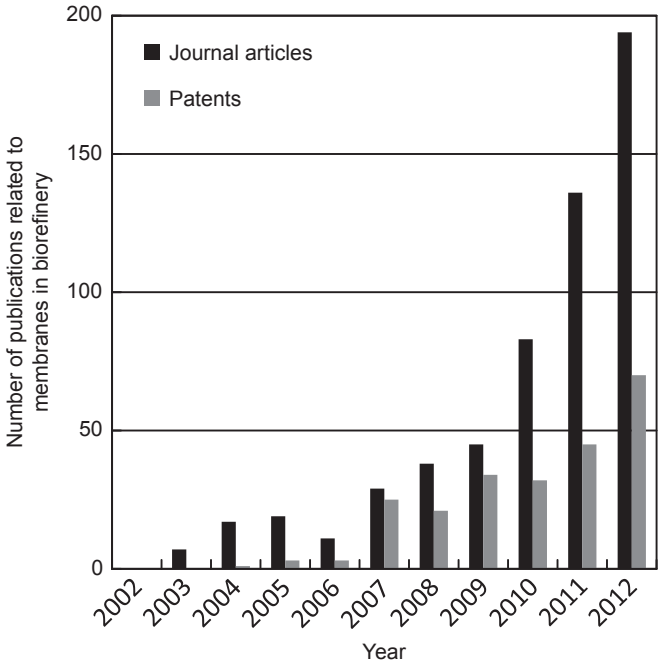

Fig. 2. Publications of journal articles and patents related to membranes in biorefinery. Search engine for journal articles – Science Direct; Search engine for patents – Patentscope.wipo.int.

into commercialization. Then membrane extraction as further concentration driven process is discussed, followed by processes operated in a pressure-driven mode (MF, UF, NF, RO) and electro-chemical driven membrane processes (electrodialysis, electrophoresis). Finally, recent developments such as solid state fermentation with integrated membrane filtration are presented and discussed. An overview of the discussed membrane processes is given in Fig. 3.

In the conclusion section, the discussed processes and membrane applications are summarized. Our vision on future trends are given against the background of a reference process established at the RWTH Aachen University turning cellulose into itaconic acid.

2. Pervaporation processes

In this section concentration-driven membrane processes are discussed, namely pervaporation and membrane extraction. These two processes have in common that concentration differences between feed and permeate cause a driving force for mass transport across the membrane. In membrane extraction two immiscible liquids are in contact with each other inside of the membrane or at either surface of the membrane, allowing for the transfer of low concentrated solutes across the L/L interface. In pervaporation, an additional phase change occurs as the fluid feed is transferred into the vapor phase at the permeate side of the membrane. Even though a vacuum pump is applied in such a system and the mass transport increases while reducing the permeate side vacuum pressure, the mass transport is not considered as a pressure-driven process. In fact, the partial pressure difference between feed and permeate is the driving force. The mass transport through such a membrane can be described with the solution-diffusion model [29]. First pervaporation processes in biorefinery applications will be discussed followed by a section dealing with membrane extraction.

Biorefinery application	Potential membrane process
Ethanol production	Pervaporation
Bio-chemical production	Membrane extraction
Biodiesel production	Ultrafiltration
Sugar production	Micro-, Ultrafiltration
Nutrient production	Micro-, Ultrafiltration
Lignin recovery	Ultra-, Nanofiltration
Solvent recovery	Nanofiltration, Reverse osmosis
Solvent / Product desalination	Nanofiltration, Reverse osmosis
Lactic acid production	Electrodialysis
Amino acid purification	Electrophoresis

Fig. 3. Overview of the diverse biorefinery applications and respective membrane processes.

2.1. Pervaporation processes in biorefinery

Pervaporation is already an established process for the recovery of alcohols from fermentation broths and has extensively been studied over the last three decades for alcohol dehydration. Bioreactor concepts were investigated in which fermentable sugar cane or corn was processed. These processes benefit from a simple pretreatment which is mechanical crushing in the case of corn. A comprehensive overview of pervaporation research starting from 1990 to 2005 is given by Vane [30]. The review gives an overview of pervaporation systems for the recovery of liquid alcohols, for instance ethanol or butanol from diluted fermentation broth. Relevant issues such as operation of integrated systems at high temperatures which could be harmful to the cells or fouling matters are discussed extensively giving examples from the literature. Several membrane materials applied in pervaporation processes (polydimethylsiloxane (PDMS) or polyimide (PI) for instance) are listed as well, including the performance regarding flux and separation efficiency in the respective investigated system. The review concludes with a general discussion of the energy efficiency and the economics of pervaporation coupled to a bioreactor.

A process scheme of a bioreactor producing ethanol with integrated pervaporation is shown in Fig. 4. In such a set-up, micro- or ultrafiltration membranes are employed downstream of the bioreactor to recover a stream of diluted fermentation broth by retaining the cells with ethanol mass fractions of up to about 10 wt% in the product stream. Then two different pervaporation processes A and B are applied to recover pure ethanol from this stream.

In this overall process (a) a hydrophobic membrane is used to separate the low concentrated ethanol from the aqueous solution. The ethanol removed from the broth cannot inhibit the reaction and valuable broth can then be fed back to the fermentation broth.

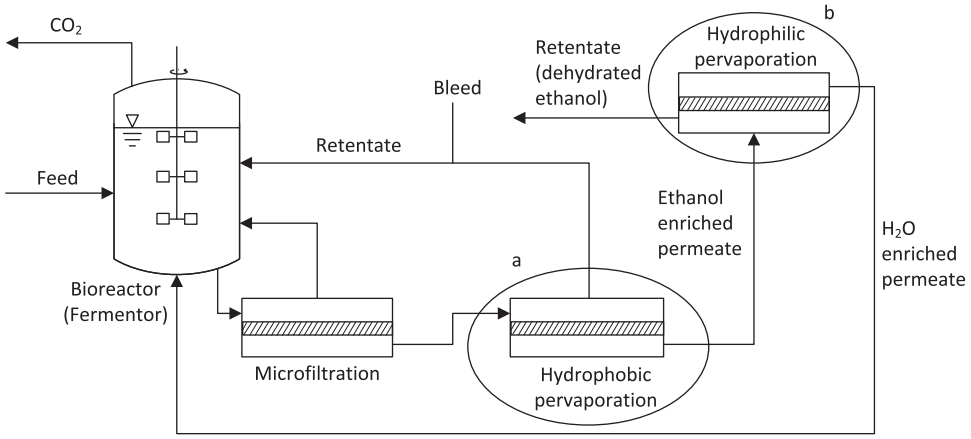

Fig. 4. Scheme of a biofuel production process utilizing untreated corn/sugar cane. Pervaporation (PV) membranes for process (a) are discussed in Section 2.2, pervaporation membranes for process (b) are discussed in Section 2.3.

Then the ethanol enriched permeate is led to the pervaporation process (b) including a hydrophilic pervaporation unit to dehydrate the ethanol. Typical feed concentrations are about 80–90 wt% and the desired product purity is not less than 99 wt%. The hydrophilic membrane helps to overcome the azeotropic composition of the mixture. Often a thermal process for the concentration of ethanol between process (a) and (b) (not shown in Fig. 4) has to be included, because the alcohol concentration in the permeate downstream of the first hydrophobic pervaporation process is too low to be fed directly into the pervaporation process. Sophisticated integrated processes of stripping/distillation coupled with pervaporation are discussed in Section 2.3.

The reported publications often address two different purposes: (a) the study of an integrated system for alcohol removal from the fermentation broth with focus on phenomena such as membrane fouling induced by the fermentation broth or equilibrium alcohol concentration in the fermentor and (b) the development of high-performance hydrophilic pervaporation membrane materials to enhance the separation performance and permeate flux of residual water from highly concentrated ethanol.

2.2. Pervaporation for alcohol recovery from fermentation broths

In this section recent publications are discussed which make use of pervaporation membranes in fermentation broth systems (Process (a) in Fig. 4). Most of these publications focus on the long-term stability of the investigated pervaporation process.

Already in 1986 Mulder et al. reported the application of pervaporation membranes for the continuous recovery of ethanol from a fermentation broth [31]. They used dense polymeric silicone rubber membranes to recover ethanol, *i*-propanol and *n*-propanol from aqueous solutions with alcohol mass fractions of about 5 wt%. They achieved selectivities ranging from 5 to 20 and permeation rates of 0.013–0.015 kg m^{-2} h^{-1}. Another trend-setting work was published by te Hennepe et al. who tested silicalite filled silicone rubber membranes for their selectivity towards alcohol [32]. Such membranes are still discussed and developed as so-called Mixed Matrix Membranes. Te Hennepe found that the incorporation of silicalite zeolites improved the membrane performance significantly. Experimental results for aqueous solutions containing 5–5.5 wt% of respectively methanol, ethanol and *n*-propanol showed that overall permeate fluxes of 0.05–0.2 kg m^{-2} h^{-1} with selectivities of up to 40 (for n-propanol) were possible.

Qureshi et al. discussed the possibility of continuous product removal from a fermentation broth by application of diverse separation techniques, such as stripping, extraction, perstraction (membrane extraction) and pervaporation [33]. Continuous substrate feeding was applied to a batch fermentation process using freely suspended cells for acetone–butanol–ethanol (ABE) production. To avoid the product inhibition which normally restricts ABE production to less than 20 g L^{-1} and sugar utilization to 60 g L^{-1}, the above named techniques were integrated into the fermentation process in order to remove the product continuously. After comparison of the diverse separation techniques the authors concluded that pervaporation was the most promising technology to process fermentation broths. In recent publications, especially the long-term operation of this technique is in focus, when working with real fermentation broths.

Gagné used a new mutant of *Saccharomyces cerevisiae* for the co-production of fructose and ethanol from sucrose [34]. The bioreactor was coupled with a pervaporation membrane module which comprised silicone-rubber hollow fibers operated in the inside-out mode. Batch fermentations were carried out with and without membrane separation of ethanol. Starting with a feed solution containing 31 vol% of ethanol the batch fermentation without coupled pervaporation required about 27 h, while with membrane separation of ethanol only 16.5 h were needed. Without membrane separation, a fructose yield of 99% and an ethanol yield of 78% was reached. With membrane separation values of 96.5% for fructose and 79.5% for ethanol were obtained.

Fadeev et al. prepared membranes which they later tested in coupled applications with fermentation broth [35,36] as well. Poly [1-(trimethylsilyl)-1-propyne] (PTMSP) membranes were prepared and pervaporation and sorption of n-butanol–water mixtures was studied. PTMSP — a hydrophobic material with an exceptionally large free volume — was assumed to be more permeable than silicone rubber at least for butanol. As the butanol concentration in the feed increased from 0.35 wt% to 0.5 wt%, the water flux dropped by a factor of about 2 and the separation factor increased by a factor of 1.7. This behavior was explained by a molecular sieve model in which the butanol molecules are supposed to block the micro-porosity within the membrane and hinder the smaller water molecules to pass the pores. Then Fadeev investigated the pervaporative recovery of ethanol from yeast fermentation broth using these PTMSP membranes in long-term experiments for about 400 h. Here the deterioration of membrane performance in the presence of fermentation broth was observed as well. The fouled membrane was characterized by gas permeation and density measurements. Sorption of pure components of the fermentation broth in PTMSP was studied to determine their fouling potential. It was found that the free volume of the PTMSP membrane was occupied by the highly sorbing, low-volatile side-products of the fermentation broth, most likely with diols.

Volkov et al. presented pervaporation data obtained for PTMSP membranes which they synthesized under various conditions [37]. They studied a multi-component organic mixture containing the major components of a yeast fermentation broth, namely ethanol (6 wt%), acetic acid (1 wt%), methyl acetate (0.5 wt%), *n*-butanol (0.2 wt%), and acetone (0.2 wt%). They found that the multi-component mixture caused deterioration of the membrane properties. The permeation rate declined over time and did not reach steady state even after 250 h. In the case of binary ethanol/water mixtures, a combination of high permeation and high separation factors (not less than 15) was measured for all PTMSP samples.

A new pervaporation membrane was recently investigated by Izák et al. [38]. A mixture of ionic liquid (15%) and PDMS (85%) was filled into a ceramic ultrafiltration membrane. This liquid membrane proved to be stable and selective in a pervaporation experiment where the membrane was coupled to the fermentation process for the recovery of butanol. These experiments were repeated with increased butanol concentration to analyze the effect on the cells. When pervaporation was switched off, the butanol concentration became lethal for the cells proving the effectiveness of the pervaporation process. The mixed IL–PDMS membrane showed high stability and selectivity removing butanol and acetone from the fermentation broth more effectively than conventional processes. The selectivity for acetone was found to be 6.77 at 5.25 g L^{-1}, while for 1-butanol the selectivity reached 11.93 at 5.71 g L^{-1}. In a long-term experiment of about 500 h the membrane allowed for a continuous product separation from the broth.

Another class of membranes which can be applied for recovery of ethanol from aqueous solutions are hydrophobic zeolite membranes, for instance silicalite-1 [43]. Lin et al. produced silicalite membranes by a single-hydrothermal synthesis on seeded porous tubular supports [44]. The silicalite seed particles provided nucleation sites, enhancing silicalite crystal growth in all directions onto the support. In result, a thin and dense crystal layer was formed. The selectivity of these membranes for ethanol over water increased by increasing the temperature during synthesis. Conversely, their permeabilities decreased. It was concluded that under higher temperatures the

growth of silicalite crystals was much faster, resulting in thicker crystal layers.

Alternatively, ZSM-5 zeolite membranes can be used to separate ethanol from aqueous solution. Such a membrane was prepared and tested on its separation performance by Weyd et al. [45]. In this publication the authors prepared a multilayered ceramic supporting membrane which allowed for the concentration of ethanol of up to 84 wt% starting with a feed concentration of 5 wt%. High permeate fluxes of up to 1 kg m^{-2} h^{-1} were achieved. This excellent permeability was explained by the homogeneous structure of the membrane characterized by uniform crystals, allowing for a straight permeation of the respective molecules.

Li et al. tested Ge-ZSM-5 zeolite membranes on their performance regarding the separation of acetone from aqueous solution [46]. In their study a permeate flux of 0.68 kg m^{-2} h^{-1} was achieved with a selectivity of 330 for an aqueous feed solution containing 5 wt% acetone.

Huang et al. prepared a composite membrane by deposing a thin-film layer of vinylmethylpolysiloxane and silicate-1 particles (size 0.1–0.2 μm) onto a porous polyether-imide membrane [47]. The silicate-1 particles were previously evaluated for their solvent adsorption capacity. The influence of membrane characteristics was experimentally determined by pervaporation experiments with n-butanol–water mixtures giving following results: (1) an increase of silicate-1 particles in the film resulted in an increase of membrane selectivity, (2) a reduction of the active-layer thickness resulted in a slight decrease of membrane selectivity and an increase of n-butanol flux, (3) a raise of the temperature induced a flux increase, but no continuous increase of the selectivity. A pervaporation experiment with fermentation broth showed that the membrane was not fouled and could be easily cleaned by using a distilled water rinse.

Qureshi et al. published their results on pervaporation with a silicalite–silicone mixed-matrix membrane in a fermentation broth [41]. The silicalite membrane was exposed to the fermentation broth for 870 h. The broth was pre-filtered with a 500 kDa ultrafiltration (UF) membrane in order to reject the bacteria. The cell-free UF permeate contained acetone and butanol which were recovered from the filtrate using a silicalite–silicone membrane. The volume removed during pervaporation was replaced with sterile distilled water. Ten successive fermentations were run with recycles from the pervaporation process. The authors noted that butanol and acetone could be extracted from the fermentation broth by applying pervaporation while the undesired side-product ethanol was retained. The rejection of ethanol was explained by its very low concentration in the fermentation broth which was below 0.4 g L^{-1}.

Nomura et al. investigated the ethanol recovery by pervaporation of fermentation broth with silicalite membranes [39]. They observed a linear increase of permeate flux with increasing ethanol feed concentration. A high ethanol selectivity was reached as well, allowing for the concentration of ethanol of up to 80 wt% in the permeate starting with an ethanol concentration in the broth of about 5 wt%. During long-term permeation experiments over 48 h the total permeate flux significantly decreased while the selectivity remained constant.

Ikegami et al. first prepared a new silicone rubber-coated silicalite pervaporation membrane and than studied its long-term behavior in an ethanol fermentation broth [40,48]. The recovery of fermented ethanol from medium by pervaporation was started after 12 h of fermentation, when about 3 wt% of ethanol had been produced in the medium. About 40 h of continuous ethanol removal helped to keep the ethanol concentration in the fermentation broth low, while the total recovery of ethanol decreased during operation time. Two reasons for this phenomenom were found: (1) the feed concentration of ethanol in the fermentation broth decreased during operation, leading to a lower recovery of alcohol (assuming a constant selectivity and permeability) and (2) glycerol acid and succinic acid, which were also present in the broth, fouled the membrane during operation time. With these results in mind the authors proposed to prevent fouling by adding activated carbon to the fermentation broth or to shift the pH.

In the publication of Chang et al. composite membranes of silicone/PVDF were prepared by curing a co-polymer of polydimethylsiloxane and phosphate ester casted on porous PVDF substrate [49]. A polymeric layer was formed on the top surface of the PVDF membrane by plasma induced polymerization. Membranes with different thicknesses of PDMS layer were produced with this method and their separation factors and permeation rates for ethanol–water mixtures were tested. The synthesized composite membranes exhibited an excellent ethanol permselectivity, particularly in the low ethanol concentration range. A separation factor of 31 and a permeation rate of 0.9 kg m^{-2} h^{-1} was reached at 10 wt% ethanol feed concentration. An overview of yet investigated fermentation/pervaporation systems is given in Table 1.

2.3. Pervaporation of highly concentrated alcohol

Hydrophilic pervaporation membranes allow for the dehydration of water/alcohol mixtures. In principle, two different types of membranes can be applied: (1) zeolite-based membranes, for instance FAU or LTA and (2) polymeric composite membranes with polyvinylalcohol or polyimide as active layer. Such membranes can be applied to separate water from highly concentrated alcohol (> 85%), as shown in Fig. 4, process (b).

In their comprehensive review Wee et al. listed several zeolite materials for the dehydration of alcohols, such as NaA, Silicalite or Mordenite [50]. Most of these materials were supported by an α-Al_2O_3 porous support membrane. Representative results for such membranes are shown in Table 2. In the review of Caro et al. the application of hydrophilic LTA zeolite membranes for the

Table 1
Overview of operation times in coupled fermentation/pervaporation systems.

Substrate	Type of microorganism	Alcohol (product)	Membrane material	Total fermentation time (h)	Ref.
Glucose	*Saccharomyces cerevisiae*	Ethanol	PTMSP	400	[36]
Glucose	*Saccharomyces cerevisiae*	Ethanol	Silicone rubber	24	[34]
Glucose	*Saccharomyces cerevisiae*	Ethanol	PTMSP	250	[37]
Glucose	*Clostridium acetobutylicum*	ABE	Supported Ionic Liquid	500	[38]
Glucose	*Saccharomyces cerevisiae*	Ethanol	Silicalite–silicone mixed-matrix	50	[39]
Glucose	Saccharomyces cerevisiae	Ethanol	Silicalite–silicone mixed-matrix	48	[40]
Glucose	*Clostridium acetobutylicum*	ABE	Silicalite–silicone mixed-matrix	310	[41]
Hydrolyzed corn fiber	*Escherichia coli* KO11	Ethanol	Silicalite–silicone mixed-matrix	120	[42]

Table 2
Overview of investigated membrane materials in pervaporation processes for pervaporation of highly concentrated alcohol.

Type	Active layer	Alcohol	Concentration feed (wt%)	Flux (kg m^{-2} h^{-1})	Separation factor α	Ref.
Zeolite	LTA	Ethanol	95	7	> 10,000	[51]
Zeolite	NaA	Ethanol	90	0.8-1	8500	[59]
Zeolite	TiO_2	Ethanol	90	1.00	800	[60]
Zeolite	TiO_2	Butanol	95	1.00	1000	[60]
Zeolite	Mordenite	Ethanol	90	0.16	139	[61]
Zeolite	Mordenite	Ethanol	85	0.06	60	[62]
Zeolite	NaA	Propanol	95	1.67	> 10,000	[63]
Ceramic	Silica	Propanol	90	8.2	NA	[64]
Polymer	Polyimide	Ethanol	90	0.02	1600	[65]
Polymer	Polyimide	Ethanol	90	1.7	240	[66]
Polymer	Polyacrylic acid	Ethanol	90	1.0	8.5	[67]
Polymer	Bacterial cellulose	Ethanol	70	0.11	287	[68]
Polymer	Cellulose-ester with perfluoro coating	Ethanol	5–95	0.3–3	65	[69]
Polymer	Polyimide	Propanol	96	1.0	900	[70]
Polymer	Polyimide	Propanol	85	0.4	3866	[71]
Polymer	Polyimide	Propanol	85	0.8	10,585	[72]
Polymer	Polyimide	Propanol	85	4.0	11	[73]
Polymer	Polyamide-imide/polyetherimide	Propanol	85	0.7	800–1000	[74]
Polymer	Polyamide-imide/polyetherimide	Ethanol	85	0.6	800–1000	[74]
Polymer	Polyamide-imide/polyetherimide	1-Butanol	85	0.9	800–1000	[74]
Polymer	Poly(vinyl alcohol)/TiO_2	Propanol	70–90	0.16–1.6	16.5-∞	[75]
Polymer	Poly(vinyl alcohol)/Zeolite 4A	Ethanol	76	0.54–4.2	25–710	[76]
Polymer	Poly(vinyl alcohol)/Chitosan	Propanol	50–95	0.1–5.0	1–817	[77]
Composite	Chitosan/CA	Ethanol	90	2.34	36.2	[78]
Composite	Chitosan/HEC	Ethanol	90	0.1	10,500	[79]
Composite	Chitosan/HEC-CA	Ethanol	90	0.4	5469	[80]
Composite	Chitosan/PES	Propanol	85	1.6	200	[81]

separation of water from organic solutions is reported [51]. These membranes show outstanding performances for the dehydration of ethanol. The reported permeate fluxes are about 7 kg m^{-2} h^{-1} with separation factors of about 10,000 for feed concentrations of 90 wt% ethanol solution. Hydrophilic zeolite membranes made of NaA were successfully produced as well and applied in an industrial process. Morigami et al. report the application of 16 pervaporation modules in a multi-purpose plant for de-hydration of alcohols [52]. These membranes offered the purification of alcohols from 90 wt% to 99.8 wt%. LTA zeolite membranes have also reached the commercial state [53]. Zeolite membranes in general offer outstanding performances regarding flux and separation factor. Nevertheless, the material is expensive. Thus, polymeric membranes, i.e. polyvinylalcohol based composite membranes, are since decades the dominant player in the field of hydrophilic pervaporation.

For zeolite membranes, the separation of water molecules from alcohol molecules can be explained by strong interactions between the water molecules and ionic sites in the zeolite crystal lattice and the partial sieving achieved by the zeolite channels [54]. Macroscopic transport equations describing the mass transfer through such composite membranes are often Maxwell–Stefan based [55]. For polymeric membranes Wijmans et al. presented the solution-diffusion model as applicable theory for mass transport during pervaporation [56]. Maxwell–Stefan formulations of this model are also available [57,58].

Jiang et al. focused on polyimide (PI) membranes for pervaporation purposes, because they can be easily modified by changing the degree of cross-linking or polymer blending [82]. In their review, the following three fields of interest were stated: (1) dehydration of organic solvents, (2) removal of trace organic compounds from water and (3) separation of organic/organic solvent mixtures. In a large literature review the authors first cited published performance data regarding flux and separation performances for polymeric membranes which are not made of polyimide and compared them to polyimide membrane performance data. They concluded that polyimide membranes can outperform other polymers especially in *i*-propanol dehydration.

Huang et al. prepared perfluoro-coated membranes for a high selectivity of water, especially at high water feed concentrations [69]. They found like many others before that the water flux for water/ethanol mixtures through hydrophilic cellulose-ester membranes was strongly dependent on the feed composition. This was explained by swelling of the membrane due to the absorbed water. By coating the base membrane with a hydrophobic perfluoropolymer the degree of swelling could be reduced and with it the amount of absorbed water. By applying the coating the water/ethanol selectivity could be stabilized to a value of about 65, independent of the feed composition. The permeance of such coated membranes was about 0.3–3 kg m^{-2} h^{-1}, depending on the thickness of the perfluoropolymer layer. It was independent of the feed composition as well.

Wang et al. developed novel dual-layer polyamide-imide (PAI)/polyether-imide (PEI) hollow-fiber membranes with the aim to avoid swelling as well as a related performance decrease during operation time [74]. Dehydration of C1–C4 alcohols was conducted and fluxes and permeances were analyzed. In result, the newly developed PAI/PEI dual-layer hollow-fiber membranes outperformed most other polymeric membranes for the dehydration of IPA and several butanols. In addition, the dual-layer hollow-fiber membranes exhibited a good long-term stability for up to 200 h operation time.

Composite hydrophilic pervaporation membranes were prepared from chitosan (CS) blended with hydroxyethylcellulose (HEC) using cellulose acetate as a porous support by Jiraratananon [80]. The membrane with a CS/HEC blend ratio of 3/1 exhibited the highest pervaporation separation index (PSI) and was selected to be cast on a porous CA support. Such produced membranes were tested with respect to their dehydration performance of ethanol/water mixtures. An increase of temperature, feed flow rate, and feed concentration enhanced the flux, but reduced the separation factor. Operating the pervaporation system at low permeate vacuum pressures resulted in increased permeate fluxes and separation factors as predicted by the solution-diffusion model.

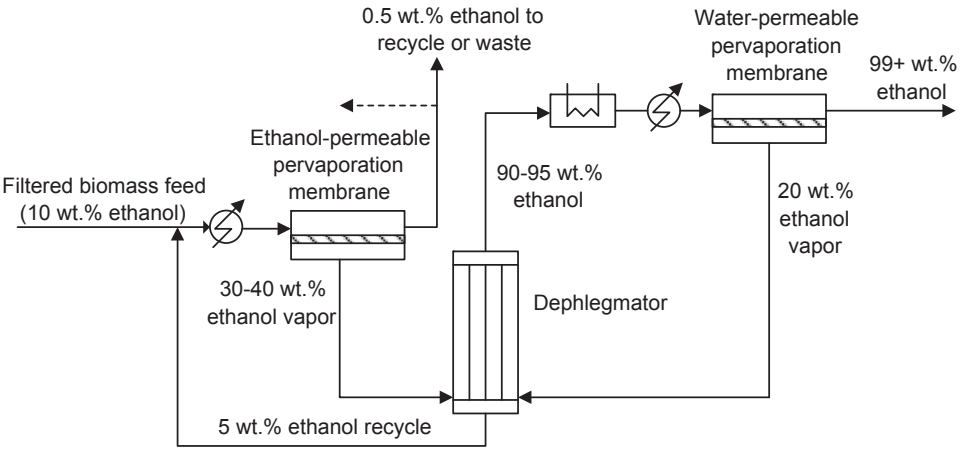

Fig. 5. Ethanol purification via dephlegmation coupled with pervaporation.

2.4. Recovery of (bio-) ethanol via distillation/dephlegmation coupled with pervaporation

Above mentioned references focused on materials and membrane developments, however the integration into a chemical process is at least as important. Fig. 5 demonstrates a recent development of an all-membrane process to turn a 10% ethanol solution into 99+% ethanol. The ethanol enriched permeate from the first pervaporation module is fed directly to a second pervaporation module to yield highly purified ethanol. If the (bio-) ethanol production side is already equipped with a distillation column to recover ethanol from the fermentation broth, pervaporation can be implemented in the existing process to lower the energy consumption considerably. Huang and Vane presented a very similar process — the so-called Biosep process — in 2006 which allows for an energy-efficient recovery of (bio-) ethanol by a coupled dephlegmation/pervaporation process [83]. Its principle is shown in Fig. 5.

It includes two pervaporation units, one upstream to recover ethanol from the fermentation broth and one downstream to purify the product stream. Upstream, an ethanol selective membrane is used to provide an ethanol enriched stream with ethanol contents of about 30–40 wt%. This stream is then directed to a dephlegmator unit. In the dephlegmator the vapor is cooled until the water condenses and flows into the bottom of the column. The ethanol enriched vapor leaves the dephlegmator with a concentration of ethanol of about 90 wt%. In this concentration range thermal devices are effective to separate water from ethanol. At higher concentrations a thermal separation of ethanol/water mixtures becomes difficult due to the azeotropic point at 96 wt% of ethanol. Hence, a hydrophilic pervaporation membrane is implemented to overcome the azeotrope and to increase the ethanol concentration to about 99 wt%. For the operation of the dephlegmator the hydrophilic pervaporation unit plays the role of a selective condenser which otherwise had to be installed for control of the reflux ratio. Thus, this combined process is more energy efficient in recovering ethanol from biomass than the conventional process without hydrophilic pervaporation membrane.

Another publication which discusses this process in detail is presented by Haelssig et al. [85]. The authors used a pilot-scale system including commercial NaA zeolite membranes to determine the influence of permeate pressure, feed flow rate, reflux ratio and further parameters on the ethanol/water flux through the pervaporation membrane. These data were used to set up a solution-diffusion-model of the pervaporation membrane. In addition a simplified model of the dephlegmator/distillation column was set up allowing for a simulation and optimization of the complete downstream process for the recovery of ethanol from a fermentation broth. With respect to the simulated results the authors concluded that the risk of flooding for the dephlegmation unit has to be taken into account and that the pervaporation membrane which allows for the concentration of ethanol to purities above 99 wt% should not be fed with ethanol streams containing less than 70 wt% of ethanol concentration.

A process concept coupling a distillation column with two pervaporation membranes was designed by MTR Inc. in 2010 [84,86]. Here the liquid process stream obtained from the fermentation broth is directly led to the distillation column (see Fig. 6). The vapor leaving the top of the column is enriched on ethanol with concentrations of about 64.7 wt%. This ethanol enriched stream is fed to two hydrophilic pervaporation membrane units and tep-wise concentrated to 99.7 wt%. Again, the application of a pervaporation membrane unit at the top of the thermal device leads to a reduction of energy consumption due to the replacement of a condenser. In fact, both membrane modules are fed with vapor streams. Thus, the membrane modules are not operated as classical pervaporation units. Nevertheless, their operating conditions are derived from pervaporation experiments with respective water/ethanol mixtures [86]. In a further publication MTR Inc. proved the feasibility of this concept by running a small scale stripping column with a 2″ diameter spiral wound pervaporation membrane module [87]. The experimental data show, that energy savings — here in the form of steam addition to the bottom of the stripping column — of 50% can be achieved by application of the pervaporation module.

Pervaporation of bio-chemicals, especially of ethanol, has already been studied in the past 30 years. Today's investigations aim at improvements of already established membranes and processes. In several publications the long-term stability of diverse hydrophobic membranes for product recovery from a fermentation broth was proved. Several membranes allow for a continuous operation over several days or even weeks. Another subject of interest is the concentration factor which allows for the recovery of up to 84 wt% of ethanol from 5 wt% ethanol in the feed solution in the case of the multi-layered ZSM-5 membrane [45].

In the field of product dehydration zeolite and polymer membranes compete for the best performance regarding permeate flux and separation factor. The separation factors obtained for the zeolite membranes are unmatched, but the materials are quite expensive making them unattractive for a swift

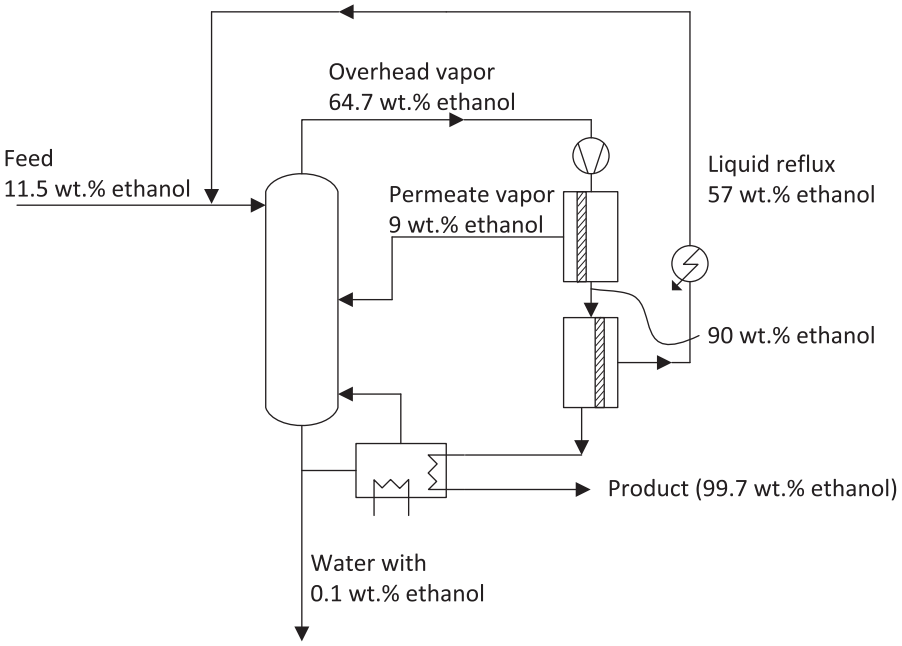

Fig. 6. Ethanol purification via distillation coupled with pervaporation [84].

commercialization. The polymer membranes allow for an inexpensive dehydration of feed solutions containing up to 15 wt% of water with average permeate fluxes.

Currently, pervaporation membranes are implemented in conventional process designs to minimize the energy consumption of thermal unit operations such as dephlegmation or distillation. Up to now, pervaporation membranes have just been added to conventional processes and did not replace them. With the recent developments in membrane preparation in mind it seems to be possible that product recovery from a fermentation process (most likely ethanol) could be performed exclusively with pervaporation membranes (see Fig. 4).

2.5. Pervaporation in a lignocellulosic biorefinery

Lignocellulosic raw material is usually pretreated before it is fed to fermentation. The pretreatment can comprise a thermal, chemical and/or enzymatic hydrolysis of the raw material to release sugars such as glucose or xylose. These can than be fermented to the respective product. During thermal/chemical pretreatment several side-products emerge such as furans, phenols or carboxylic acids. Most of these side-products are toxic for the fermenting microorganism which results in a decreased productivity. Some of the side-products, especially furfural are not just toxic compounds regarding the fermentation, but valuable chemicals as well [88]. Therefore, some new publications focus on the removal or recovery of these molecules from hydrolysates or broth effluents via pervaporation.

A polyurethaneurea (PUU) polymer membrane was prepared by Ghosh et al. [89,90] by casting a viscous poly-urethaneurea solution over a glass Petri dish. With such produced flat-sheet membranes pervaporative separations of furfural/water mixtures were performed. The swelling of poly-urethaneurea membranes in aqueous furfural solution at different furfural concentrations and different temperatures was studied with the result that the membrane swelling varied with soft segment content of poly-urethaneurea. The effect of feed composition on permeate flux (total as well as individual) was investigated over the furfural concentration range of 1.0–6.0 wt%. The membranes were found to be highly furfural selective, with furfural separation factors as high as 638 and a permeate flux as high as 44.7 g m^{-2} h^{-1}. The total flux was found to increase with temperature and concentration of furfural in the feed.

O'Brien first proved the economic relevance of pervaporation for commercial-scale fuel ethanol plants before investigating the technical feasibility of ethanol recovery from corn fiber hydrolysate fermentations [42,91]. Corn fiber was hydrolyzed by dilute sulfuric acid and neutralized by either conventional lime treatment or neutralization with strong basic solutions prior to the fermentation step. The hydrolysate was processed to an anion exchange resin to remove toxic compounds such as furfural, HMF or acetic acid. Then fed batch fermentation was performed with the neutralized and detoxified hydrolysate. During the fermentation the ethanol concentration remained below 25 g L^{-1} with complete sugar utilization for approximately 5 days. Then pervaporation was performed to recover the products. A concentrated ethanol stream of 17 wt% ethanol was obtained from the pervaporation unit. The membrane area in the pervaporation module was 0.22 m^2. Pervaporation resulted in a concentrated permeate stream of 150–170 g L^{-1} ethanol.

Sagehashi et al. studied the separation of phenols and furfural from biomass hydrolysates via pervaporation [92]. The aqueous feed solution was obtained from superheated steam, stemming from a biomass pyrolysis process. Three different silicone rubber membranes, providing thicknesses of 40, 100 and 200 μm were used in the pervaporation experiments. The total flux was found to be inversely proportional to the membrane thickness, whereas the separation factor remained constant at about 60 for a temperature of 60 °C. Further experiments with the 200 μm membrane showed that all three separation factors for furfural, phenol and guaiacol were between 20 and 70 under temperatures of 40–120 °C. The best separation factors were obtained for 60 °C. The total permeate fluxes followed an exponential growth which could be best described with the law of Arrhenius. The maximum values were 104 g m^{-2} day^{-1} for guaiacol, 53 g m^{-2} day^{-1} for furfural and 38 g m^{-2} day^{-1} for phenol at 120 °C.

In their study Gaykawad et al. explored the pervaporation of ethanol stemming from a lignocellulosic fermentation broth [93]. They used pretreated nutrients such as barley straw or wood chips to feed a fermentation broth from which they recovered ethanol

via pervaporation. Thus, the aim of the study was to determine the influence of raw material and pretreatment method on the ethanol production. The raw material was pretreated with sulfuric acid at varying concentrations. The employed yeast cell *S. cerevisiae* was supposed to be inhibited by diverse compounds from the raw material such as furfural, 5-HMF or acetate. The highest glucose concentration of 70 g L^{-1} in the nutrient solution was obtained for the pretreatment of barley straw with concentrated acid. Therefore, the highest product formation of about 30 g L^{-1} of ethanol was reached by feeding this nutrient solution to the fermentation. The pervaporation experiments for the recovery of ethanol were carried out with a commercial PDMS membrane. For characterization purposes pervaporation experiments were initially carried out with ethanol/water mixtures. These results were than compared with ethanol, respectively water fluxes from a broth effluent. The authors found that the presence of 5-HMF in the effluent decreased the water flux without affecting the ethanol flux during pervaporation. Furfural increased both water and ethanol fluxes, resulting in a better selectivity for ethanol. The adsorption of the diverse compounds on the membrane surface caused an increase in fouling of about 20% in comparison to an ethanol/water model solution.

Cai et al. performed a fermentation of sweet sorghum bagasse hydrolysate with subsequent pervaporation to recover butanol and acetone [94]. First, the raw material was grinded and pretreated with dilute acetic acid in a pressure tank. The hydrolysate was heated up and fed to a pervaporation module prior its fermentation with *Cerevisiae aceotbutylicum*. The employed membranes were made of PDMS. Hereby the furfural, which originated from the pretreatment process, was removed to detoxify the nutrient solution. The furfural concentration could be lowered by the pervoparation from about 10 g L^{-1} to about 0.6 g L^{-1}. Then the detoxified hydrolysate was fed to the fermentration broth. A control experiment with glucose nutrient solution revealed that despite the same total sugar content the fermentation of the pretreated raw material resulted in a lower product formation. This result was explained with the presence of toxic side-products from the pretreatment process beside furfural, for instance phenols. Nevertheless, the reduction of product formation by fermenting the pretreated raw material was marginal. The authors concluded that the pervaporative removal of furfural prior the fermentation is crucial and sufficient for detoxification of the hydrolysate.

Liu et al. investigated the ability of a newly developed nanocomposite membrane to recover furfural from aqueous solutions via pervaporation [95]. The membrane comprised a metal-organic framework into which a homogenous ZIF-8-silicone rubber layer was placed. The authors called the production technique "plugging–filling method", because they first plugged ZIF-8 nanoparticles onto the metallic framework and then filled PMPS rubber into the support to obtain a dense layer. The ZIF-8 particles allowed for an exclusive permeation of furfural molecules from a furfural/water mixture. Selectivities of up to 10 were obtained for the recovery of furfural from an aqueous solution with 1 wt% of furfural.

In summary, we conclude that a change of fermentation feedstock from glucose solution to pretreated lignocellulosic raw material leads to an increased demand of downstream processing. Two objectives are from interest: (1) removal of inhibitory side-products from the nutrient solution in order to maintain the productivity of the fermentation and (2) recovery of inhibitory side-products which are valuable chemicals themselves, for instance furfural.

2.6. Membrane extraction

The principle of membrane extraction, sometimes called perstraction, is shown in Fig. 7. Typically, a hollow fiber module is applied comprising a bundle of hydrophobic membranes (made of PVDF or polypropylene for instance). Spiral-wound modules could be applied as well, but no commercial products are available up to now [96]. Due to their abundant availability organic solvents such as n-heptane are first choice, but alternative solvents such as ionic liquids can be utilized as well [97]. In comparison to a conventional extraction, which is carried out by simply mixing the two immiscible fluids, membrane extraction offers following advantages: (1) the membrane — usually a micro- or ultrafiltration membrane — provides a large surface area to bring the aqueous phase in contact with the extractant. Each pore allows for the diffusive transfer of product from the feed solution into the extractant. (2) The modularity of the membrane elements allows for a continuous operation while being scalable through parallelization of the modules. (3) The transfer rate, expressed in terms of a mass transport coefficient, can be optimized by adjusting the volume flow ratio. The mass transport coefficient specifies the velocity of the transferred solute through the membrane and

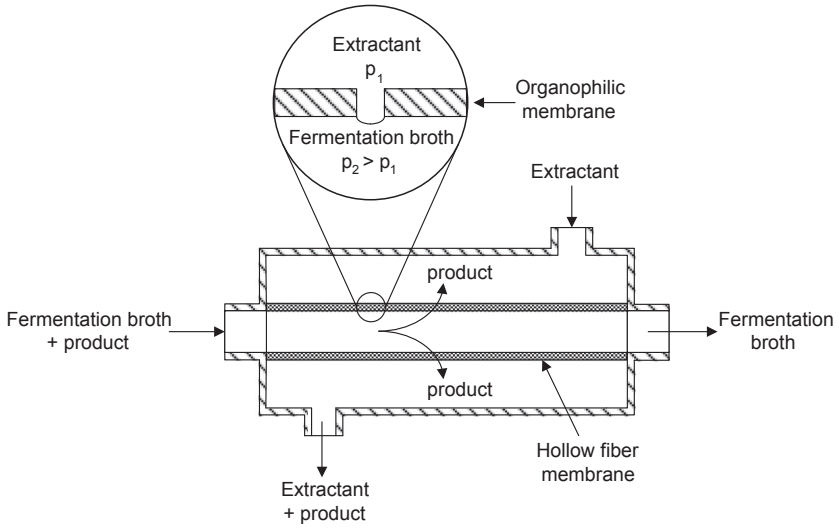

Fig. 7. Principle of membrane extraction for the recovery of product from a fermentation broth. In this case the fermentation broth flows through the lumen of the membrane.

depends on the membrane, the hydrodynamic conditions of concentration polarization at the membrane surfaces, the substance system and the solute concentration difference between feed solution and extractant. A drawback of the membrane extraction process is the additional resistance of the membrane. Depending on the wetting properties of the membrane (hydrophilic/hydrophobic) either the feed solution or the extractant fills the pores of the membrane. However, the predictability and precise control of all hydrodynamic conditions is a significant advantage outweighing the loss in mass transport due to the membrane. The other fluid has sometimes to be pressurized in order to prevent breakthrough of the pore filling liquid.

Solichien et al. compared the extractive removal of propionic and acetic acid from a fermentation broth using a flat-sheet membrane module as well as a hollow fiber module [98]. They tested various porous membranes consisting of different polymers, such as polypropylene, polyethylene, polystyrene or cellophane in the flat sheet module. Several extraction solvents were tested as well, decalin, tetradecane or dodecane for instance. The best overall mass transfer coefficient was found for the combination of a polypropylene and a mixture of 10% decane with tri-*n*-octylphosphine oxide as carrier. With this combination detailed experiments were carried out in a hollow fiber module. The mass transfer coefficient was somewhat lower than for the flat-sheet module, which was explained with lower feed flow velocities leading to concentration polarization. Nevertheless, mass transfer coefficients of up to 1.08×10^{-4} cm s^{-1} for propionic acid and 3.64×10^{-5} cm s^{-1} for acetic acid were obtained.

Tong et al. studied the extraction of lactic acid from a fermentation broth with micro-porous hollow fiber membranes [99]. The extractant oleyl alcohol contained the additive tri-n-octylmethylammonium chloride which allowed for a reactive extraction of lactic acid via anion-exchange with tri-n-octylmethylammonium chloride. The fermentation broth was directly led through the membrane module without pre-filtration. An extraction of lactic acid from the broth of up to 70% could be achieved depending on the feed concentration.

Adler et al. investigated the extraction of 2-phenylethanol (2-PE) and 2-phenylethylacetate (2-PEA) from a fermentation broth with a hollow fiber module [100]. The membrane fibers were made of the hydrophobic polypropylene. The fermentation was carried out with the yeast *K. marxianus*. The fermentation broth was pumped through the hollow fibers with an overpressure of 0.5 bar, while the extractive miglyol phase was fed to the shell side. The partition coefficients of 2-PE and 2-PEA were measured to specify their distribution in the immiscible solvents at equilibrium. They were determined to 7.7 and 361, respectively. A model was set up to describe the concentration dependence of 2-PE and 2-PEA in the fermentation broth as a function of time. For the product formation an autocatalytic reaction was assumed, whereas for the extraction a pore flow model was applied. The calculations were in good agreement with the experimental data, allowing for a prediction of 2-PE and 2-PEA concentrations during the coupled fermentation/extraction. A strong dependence of the volume ratio of broth and extractant and initial aroma concentrations on the extraction performance was found.

Chang et al. studied the extraction of ethanol from a fermentation broth with the extractant dibutyl phthalate. The ethanol was produced via fermentation of the yeast *S. cerevisiae* [101]. The recovery of ethanol was carried out with two different set-ups: (1) a diafiltration membrane module with the extractant dibutylphtalat (DBP) was directly coupled to the fermentation broth and (2) an additional ultrafiltration module was placed between fermentor and extraction module in order to recycle the yeast cells into the reactor. With the first set-up the ethanol concentration could be lowered from 51 g L^{-1} to 41.5 g L^{-1}, while the glucose conversion increased from 45% to 91%. In result, the productivity of the reactor increased from 8.2 to 20 g L^{-1} h^{-1} compared to an operation without extractive removal of ethanol. The extended set-up with the additional cell rejection allowed for a productivity of even 53 g L^{-1} h^{-1} of ethanol. This effect was explained by the increased cell concentration of 63 g L^{-1} in the fermentor compared to 23.6 g L^{-1} for the first set-up including just the extraction.

Chen et al. studied the extraction of surfactin from fermentation broth of *Bacillus subtilis* with a hollow fiber membrane module [102]. *n*-Hexane served as extractant and was led through the shell side of the module. The membranes were made of hydrophobic PVDF. The authors first measured the extraction efficiency for surfactin into dispersed *n*-hexane in water and compared these results to the efficiency of a membrane extraction including the same substance system. Surprisingly, the removal of surfactin from the aqueous phase was initially faster by applying the membrane module, even though the membrane accounted for an additional mass transport resistance. Detailed investigations showed that a large amount of the surfactin molecules was adsorbed onto the membrane surface and was not extracted into the *n*-hexane phase. A model was successfully developed, taking the effect of surfactin adsorption into account.

Grobben et al. investigated the extractive removal of ABE solutions from a fermentation broth [103]. The extractants were chosen such that they also could be used as fuel. Hence, the quality of the produced biofuel cannot be diminished by residual traces of the extractant. A mixture of oleyl alcohol and decane and a fatty acid methyl ester (FAME) solution stemming from sunflower oil were tested as practicable extractants. In this case the respective extractant was pumped through the polypropylene hollow fibers, while the fermentation broth was led through the shell side with an overpressure of about 0.3 bar. A composition of 50 vol% of oleyl alcohol and 50 vol% of decane was selected due to the highest mass transfer and partition coefficients. Coupling of the membrane module to the fermentation broth significantly lowered the butanol concentration leading to an increase of ABE production of about 73%. After a certain time of operation a change in membrane wettability was observed. Thus, it was necessary to reduce the shell side pressure to about 1 bar. In order to avoid membrane fouling, a microfiltration step was included into the process to reject the yeast cells and solids prior the membrane extraction.

Grzenia et al. published several articles on membrane extraction of biomass hydrolysates [104–106]. In the first cited article the extraction of acetic acid from biomass hydrolysates was studied [104]. The acetic acid was used to pretreat the cellulose prior conversion to glucose by enzymatic hydrolysis. After the pretreatment the spent solvent had to be removed in order to not affect downstream processing. For this purpose octanol was chosen as extractant, containing varying amounts of the additive Alamine 336, a multi-functional amine. The membrane modules were designed as plate-and-frame modules which were equipped with polypropylene membranes. The transfer of acetic acid into octanol was studied with the various extractant mixtures at different flow rate ratios. Up to 60% of the acetic acid could be removed with an extractant mixture of 50% Alamine in 50% octanol.

In a further publication the extraction of sulfuric, formic and levulinic acid was studied as well as furfural and 5-hydroxymethylfurfural [105]. A hollow fiber polypropylene module was used. Octanol with Alamine 336 and mixtures of oleyl alcohol and Alamine 336 served as extractants. The extraction of the diverse compounds was carried out in batch experiments. To explain the results, the mass transfer coefficients for all substances named above were determined. The membrane was identified as limiting mass transfer resistance. Nevertheless, an efficient extraction could be realized for all substances. In a further

publication, one surface of the polypropylene membranes was modified by layer-by-layer deposition of polyelectrolytes [106]. In result the membranes became amphiphilic. Due to the modified wettability an aqueous organic interface could be stabilized within the membrane pores. With this technique the loss of organic solvent through the membrane pores could be reduced [107].

Berrios et al. studied the extraction of gibberellic acid—a plant growth promoter—from fermentation broths using emulsion liquid membranes [108]. In fact, the so-called membrane consisted of liquid droplets comprising an internal phase and an external phase. The internal phase was an aqueous solution with varying amounts of KCl and phosphate buffer while the external phase was *n*-heptane. To stabilize the emulsion, the surfactant the SPAN 80 and carrier Aliquat 336 were added to the emulsion. The extraction was then carried out by mixing this emulsion with the fermentation broth via stirring. After stop of stirring, the emulsion and the fermentation broth unmixed again within few minutes and could be easily separated. After the phase separation of the emulsion it was heated to about 80 °C in order to break the droplets consisting of n-heptane, water and extracted gibberellic acid. A second phase separation was achieved allowing for the collection of gibberellic acid from the aqueous phase. With this method about 67% of the fermented gibberellic acid could be extracted from the broth.

We conclude that membrane extraction offers the possibility to selectively remove chemicals from fermentation broths. Membrane modules are commercially available, for instance the Liqui-Cel product line. The partition coefficients determine the extraction efficiency and can be readily estimated using standard thermodynamic databases and models such as the UNIFAC model or the Non-Random Two-Liquid (NRTL) model which are for instance implemented in Aspen. Well-established mass transfer correlations can be used to estimate resistances in the boundary layers adjacent to the membrane. A comprehensive overview of possible membrane extraction module designs is given in the book of Ho and Sirkar [109].

3. Pressure-driven membrane processes

3.1. Biodiesel production from plant oil

Biodiesel consists to 99.7% of Fatty Acid Methyl Esters (FAME with FA having different lengths R1, R2, R3). It is usually obtained by transesterification of triglyceride (TG) stemming from canola oil. In a three-step reaction the triglyceride is consecutively transformed to glycerol, releasing fatty acid alkyl esters in each reaction. These esters then react with the ambient alcohol phase to the respective alkyl ester (Fig. 8).

The first choice reaction medium is either methanol or ethanol with a base or an acid as catalyst to encourage a fast and complete conversion of triglyceride to FAME. In these solvents the reaction is heterogeneous. As all reactions of triglyceride to glycerol are reversible, a continuous product removal is desired, in order to yield high conversion rates to FAME.

A cost-effective process concept is the membrane reactor presented in Fig. 9. A microfiltration membrane enables the removal of continuous phase containing the FAME product from the heterogeneous reaction phase. The product solution is initially homogeneous, but a phase separation between the FAME and methanol and a glycerin rich phase is observed after a short time delay.

In their review on biodiesel production via catalyzed transesterification Leung et al. compared membrane extraction with the more established processes of water washing and dry washing via ion exchange resins or magnesium silicate for product recovery [111]. They concluded that membrane extraction is advantageous concerning the product quality and product loss, but suffers from high equipment costs and low production rates.

Cao et al. discussed the influence of membrane pore size on the FAME yield [110]. Background of this study is the fact that triglyceride is immiscible with methanol. Hence, it forms droplets which can be retained by the membrane. The intermediate products such as diglyceride are already partially miscible. They form homogenous solutions with the methanol and can pass the membrane without reacting to the final product glycerol. Carbon membranes with pore sizes ranging from 0.05 to 1.4 μm were tested for their rejection behavior towards the triglyceride droplets and intermediates. The size distribution of triglyceride droplets was in the range of 12–400 μm.

The final reaction yield was not affected by the choice of membrane. This finding was attributed to the fast reaction rates of the homogenous intermediates. As soon as an intermediate was released from the immiscible triglyceride droplet it was immediately converted to glycerol before it could pass the membrane. The authors concluded that for a viable operation of the membrane reactor (with full conversion of the intermediates) only the triglyceride droplet size had to be taken into account for determination of the minimum pore size of the membrane. In following publications, Cao studied the influence of raw material compositions on the final FAME product [112] and the maximization of

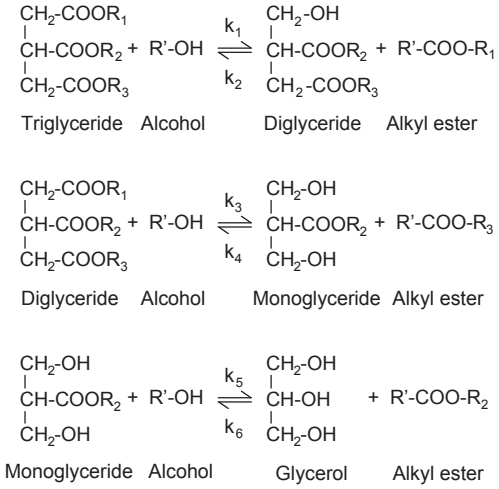

Fig. 8. Elementary reaction scheme for the transesterification of triglyceride. Taken from [110].

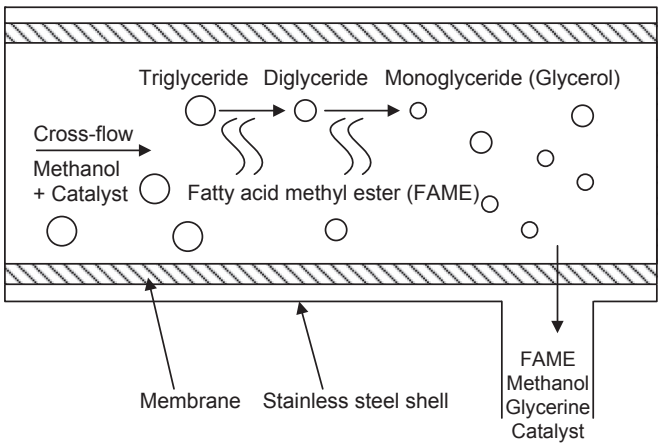

Fig. 9. Microfiltration process for the extraction of fatty acid methyl ester (FAME) from canola oil.

FAME concentration in the product stream by recycling the methanol/glycerol solution after phase separation of the product [113]. Dubé et al. studied the conversion of canola oil to FAME in a carbon membrane reactor as well [114]. This study is interesting, because a long-term operation of over 10 months is reported, where the membrane material was in permanent contact with methanol/acid or methanol/base solutions. Within this period no degradation of the membrane material was observed.

The operation of a membrane reactor including a detailed thermodynamic analysis concerning the phase behavior of the oil/FAME/methanol solutions is presented by Cheng et al. [115,116]. In these studies three-phase diagrams were utilized to determine the optimal point of operation. Accompanied by experiments, the reaction rate and the development of the respective FAME and side product concentrations in the two-phase system were determined. The authors concluded that an increase in residence time of the reactant system within the two phase zone was advantageous for the production of FAME. They suggested setting up a pre-reactor to initiate the reaction prior processing the mixture with membrane reactor. Membrane-based downstream processing of the resulting FAME product stream with methanol and glycerol as impurities was studied in several publications. Saleh et al. examined the possibility of FAME purification from glycerol in a membrane-based downstream process [117]. Again, ultrafiltration membranes consisting of polyacrylonitrile (PAN) with a MWCO of 100 kDa were chosen to separate glycerol from FAME solution. Small amounts of water were added to the FAME/glycerol mixture to yield a two-phase system. The glycerol formed small droplets which were easily retained by the membrane. Hence, the purification performance of the membrane was strongly dependent on the amount of water in the mixture.

Wang et al. [118] studied the refining of biodiesel (FAME) with ceramic ultrafiltration membranes with a pore size of 0.6, 0.2 and 0.1 μm to remove the residual soap and free glycerol from the FAME product. These compounds formed reversed micelles with a mean droplet size of about 2.2 μm. A fixed filtration pressure of 1.5 bar was applied at a temperature of 60 °C. Special focus was set on the rejection performance regarding glycerol, but also the separation of ions, such as potassium or sodium from the feed solution was studied. These substances typically originate from the transesterification catalyst. A physical understanding of the metal rejection could not be provided by the authors, but they assumed that especially the cations were somehow attached to the emulsion droplets. A model solution including all the relevant species was filtered with the ceramic membranes: the removal of all impurities was more efficient in comparison to the standard washing process with water. Gomes et al. [119] investigated the same system, but used a tubular Al_2O_3/TiO_2 ceramic membrane to separate glycerol from concentrated FAME solution and catalyst ethanol. Membranes with average pore sizes of 0.2, 0.4, and 0.8 μm were applied. The separation of glycerol from biodiesel was studied with respect to the applied pressure and the ethanol content in the feed composition. For none of the tested membranes the rejection of glycerol undercut a value of 99%, independent of the applied pressure (from 1 to 3 bar). However, a clear decrease in separation performance for glycerol was found for increased amounts of ethanol in the feed composition (ranging from 99.6% to 98.1% while increasing the ethanol feed concentration from 5 wt% to 20 wt%).

In a recent publication Baroutian et al. studied a packed bed reactor containing an inorganic membrane of TiO_2, respectively Al_2O_3, also reporting very high conversion rates [120]. The membrane served as reactor housing and separator. Within the membrane tube activated carbon, soaked with KOH solution was immobilized and served as catalyst. Aim of this publication was to optimize the FAME yield with respect to the catalyst mass fraction, cross-flow velocity and temperature. Thus, an experimental design matrix was set up and an empirical model was fitted to the experimental results. The authors concluded that the temperature was the most relevant parameter determining the product yield. Numerical calculations predicted a maximum conversion rate in this special membrane reactor of 94% at a temperature of 70 °C, 157.04 g catalyst per unit volume of reactor and a cross-flow velocity of 0.21 cm s^{-1}. Experimentally found conversion rates of 92% were in good agreement with this finding.

Recently, solvent-resistant nanofiltration membranes, such as the Starmem series from Evonik Membrane Extraction Technology (MET), the Desal membranes from GE Osmonics and the Solsep membranes were tested for their separation performance towards impurities of methanol and glycerides from the methyl ester product [121]. In this study, dry biodiesel was produced from palm olein which contained the impurities ethanol, monoglyceride, diglyceride and unreacted triglyceride. The feed solution was homogenous. Hence, nanofiltration membranes were chosen to separate the molecular impurities from the FAME product. None of the membranes provided stable permeate flux rates or rejection performances due to physical or chemical denaturation of the membranes. To overcome these stability problems, the pH of the feed solution was adjusted to 8.68 (before 12.43), resulting in a stabilized permeate flux for two Solsep membranes and the Starmem 240 membrane. A study on the selectivity of the Solsep 03075 membrane showed that a partial separation of the impurities from the FAME product was possible.

3.2. Purification of sugar cane juice

The production of sucrose from sugar cane juice includes several downstream unit operations which can be partially replaced by membrane separations. The conventional process relies on lime and sulfur dioxide addition to clarify the raw juice stemming from a sugar cane mill (double-sulfitation process). The raw juice is a complex mixture which is initially clarified by addition of sulfur dioxide and calcium hydroxide (lime). In result, the suspended colloids of the raw juice coagulate and precipitate along with calcium sulfite. The clarified juice is then concentrated by evaporation (steam heating) and bleached by a second sulfitation. At last the product stream is crystallized to obtain white sugar crystals. The double-sulfitation process suffers from

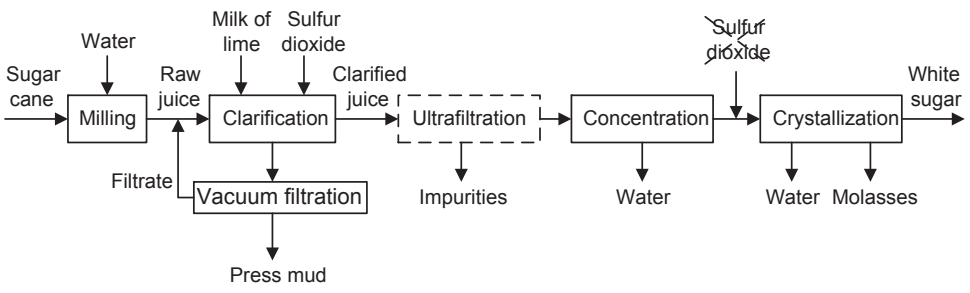

Fig. 10. Application of ultrafiltration membranes in cane sugar refining. Aim is to eliminate the second sulfitation step of clarified and concentrated sugar cane juice. Scheme adapted from [122].

inefficient removal of substances from the raw juice, like gum, ashes, silica, colorants and reversible colloids and an inefficient removal of sulfite from the product stream. In result, the quality of plantation white sugar is noticeably inferior to refined sugar [122]. Hence, ultrafiltration membranes are investigated to replace the second sulfitation step for the purification of clarified sugar cane juice (see Fig. 10). The cited publications focus on the removal of solids such as dextrans or waxes [122,123], the decolorization of raw juice, respectively clarified juice [124,125] and the permeate flux decline due to the occurrence of fouling [124,126–130].

Ghosh et al. studied the application of spiral-wound ultrafiltration modules [122,124] in order to replace the sulfitation process for raw juice clarification. The ultrafiltration process was superior in terms of decolorization and rejection of CaO. As drawback, about 10% of sugars were retained by the membrane as well. A flux decline down to about 33% of the initial value in the first 50 min was observed.

Similar investigations were performed by Balakrishnan et al. [126,127]. They also performed field trials on an actual plant with special focus on the influence of various operating parameters. The ultrafiltration process was superior to the conventional sulfitation process by means of decolorization and purification performance. Nevertheless, a strong flux decline during the first hour was observed. Operating parameters such as transmembrane pressure, feed velocity across the membrane module and the variance of pH value were taken into account. Increasing the trans-membrane pressure resulted in faster cake lake formation with subsequent permeate flux decrease. This flux decline could be reduced by varying the cross-flow velocity and increasing the pH from originally 5.5 to 11 by adding lime. Both measures reduced the cake layer formation on the membrane surface.

Balakrishnan et al. extended the study on membrane fouling during sugar cane juice ultrafiltration with special focus on the role of polysaccharides in the feed juice [130]. In this study the occurrence of fouling on polysulfone (PS) and polyethersulfone (PES) membranes in different operation modes was investigated for clarified and untreated sugar cane juice. In the static mode, the back side of the membrane was sealed with a polymeric adhesive tape to prevent any permeation. In the dynamic mode the membrane was operated in a dead-end filtration cell at pressures of up to 1 bar. With this method the contributions of surface and internal fouling could be distinguished. For all studied membranes except one fouling was increased in the dynamic mode indicating that internal fouling played a significant role. In addition, a shift to lower values of molecular weight cut off (MWCO) is reported as a consequence of fouling.

The permeate flux reduction during sugar cane juice microfiltration due to fouling was intensively modeled by Jegatheesan et al. [129]. In this study, experiments with clarifying limed and partially clarified raw sugar cane juice were carried out with ceramic membranes in order to obtain values for the flux decline during the first 4 h of operation. Four different models were fitted to the experimental results: (1) the cake filtration model, (2) pore-narrowing model, including progressive internal fouling, (3) a combination of external and progressive internal fouling and (4) a complete pore-blocking model. The authors concluded that the combination of external and progressive internal fouling described the microfiltration experiments best.

Lutin et al. applied microfiltration membranes and electrodialysis membranes to clarify diffusion juices in the starch and sugar industry [131]. They installed Scepter® microfiltration membranes in a plant producing 50 $m^3 h^{-1}$ of corn sirup juice. The juice contained max. 0.3% of total suspended solids. By replacing the rotary vacuum filters the operating costs could be lowered by 7.5€ per ton (from 13.5€ per ton). Additionally, the loss of sugar could significantly be reduced to a third by using the microfiltration membranes. Electrodialysis was carried out to demineralize the juice. About 70% of minerals could be removed with this technique.

3.3. Fermentation processes

In a fermentation based biorefinery the conversion of biomass to valuable products is performed via enzymes or microorganisms. Hence, the conversion is usually performed in aqueous environment. Pressure-driven membrane processes are applied to (1) recover the product by simultaneous rejection of microorganisms (2) to treat the (spent) fermentation broth in order to recover valuable side products. Carstensen et al. recently published a comprehensive review article about the product recovery from a fermentation broth via micro- and ultrafiltration [132]. In this review publications referring to the product recovery from fermentation broths by ultra- or microfiltration are excluded and alternative membrane processes are discussed instead.

Colón et al. studied the removal of volatile fatty acids from an anaerobic bioreactor using a 10 kDa tubular ceramic membrane module [133]. These acids acted product inhibiting during the degradation of inedible biomass via rumen bacteria. Several parameters influencing the permeate flux were studied such as filtration pressure, cross-flow velocity within the membrane module and suspended matter concentration. By increasing the pressure or the cross-flow velocity the permeate flux linearly increased, whereas an increasing particle concentration reduced the permeate flux. Removal of the acids from the fermentation broth was possible. However, valuable nutrients such as ammonium, phosphate or calcium got also lost in the permeate.

Timmer et al. studied the lactic acid separation from fermentation broths via reverse osmosis (RO) and nanofiltration (NF) [134,135]. They fermented delactosed whey powder using *Lactobacillus helveticus* 37N to obtain a product solution containing 4 wt % of lactic acid. The authors tested several RO and NF membranes at feed pressures of 10–40 bar to recover lactic acid from the broth. For all membranes the lactic acid was partially rejected. The rejections for the NF membranes varied between 50% and 70%, while the rejections for the RO membranes were significantly higher and reached values of about 80–99%. A special focus was set on the fouling behavior which was modeled to predict long-term operation of the nanofiltration membrane NF40 from Filmtec [134]. During filtration of solutions still containing yeast cells the permeate flux decreased significantly by a factor of 3 during the first 6 h of operation starting with a permeability of 0.7 $L m^{-2} h^{-1} bar^{-1}$. In a second run the product solution was pre-filtered using an UF membrane to retain the yeast cells. The permeability of such clarified solution was initially about 1.4 $L m^{-2} h^{-1} bar^{-1}$, but rapidly dropped to a value of about 0.1 $L m^{-2} h^{-1} bar^{-1}$ within the first 5 h of operation. The differences of initial permeability and flux decline were explained by different fouling phenomena affecting the membrane. While for the pre-filtered solution colloidal fouling dominated, for the untreated solution fouling was caused by a gel-layer.

In a second publication Timmer et al. developed a model to describe the permeate flux and rejection of lactic acid using NF and RO membranes, depending on the applied feed pressure [135]. The model was based on the Nernst–Planck equation and provided a good accuracy. Two mass transfer parameters and two rejection parameters had to be calculated to apply the model. For the calculation of these parameters experimental filtration results had to be known as well as substance system specific parameter, such as the equilibrium constant between dissociated and undissociated lactic acid. Therefore, the authors claimed that the model could be applied to other acids as well.

Pressure-driven membrane processes have also been applied for recovery of valuable products and/or intermediates present in the effluents from spent fermentation broth. The residue of the fermentation broth after product evaporation (typically ethanol) is called whole stillage. It contains the fiber, oil, protein, diverse unfermented components of the grain and yeast cells. In conventional processes the whole stillage is centrifuged or vacuum belt filtered and thereby separated into thick stillage and thin stillage. The thick stillage, containing mostly solids can be sold as an animal feed, called "wet distillers grains with solubles" (WDGS). The thin stillage has to be dehydrated before it can be mixed with the thick stillage to obtain a product called "dried distillers grains with solubles" (DDGS) in order to greatly lengthen the product shelf-life [136]. Drying of thin stillage is conventionally performed via evaporation, resulting in problems such as deposit formation on heat transfer surfaces. To overcome these problems membrane separations are investigated for the recovery of valuable solids from thin stillage [137].

Fig. 11 gives an example for the post treatment of thin stillage via ultrafiltration. Arora et al. extensively studied the system shown above [137–140]. The aim of these studies was to recover valuable nutrients such as ethanol, lactic acid, acetic acid and saccharides (glucose, fructose, etc.). Thus, several cellulosic ultrafiltration and microfiltration membranes were investigated on their separation performance and permeability. The ash content of the feed solutions could be reduced to minimum 50% by applying the tested membranes. Koschuh et al. studied the purification of silage juice via nanofiltration to obtain valuable lactic acid and amino acids [141]. They investigated the retention of several polymeric nanofiltration membranes and one inorganic nanofiltration membrane and found that in average of 18 investigated amino acids a retention of about 10–20% could be achieved. They concluded that NF membranes could help to purify the silage juice.

Hwang et al. examined the separation of proteins from fermentation broth by discussing the hydrodynamic influences using a model solution containing *Baker yeast* and *albumin bovine serum* flowing through a cross-flow test cell [142]. The thickness of the cake layer was calculated taking the transmembrane pressure, the cross-flow velocity and cell geometry into account. From knowledge of the cake layer built-up the degree of permeate flux reduction and rejection performance was derived.

Leberknight et al. studied the recovery of valuable side-products such as proteins in a corn to ethanol process as well [143]. In contrast to the previous studies, not the effluent of the fermentation broth, but the feed was processed via ultrafiltration. The intention was to recover valuable proteins as soon as possible from grinded corn solution. Hence, protein denaturation during the distillation of the silage after fermenting could be avoided. For this purpose PES and regenerated cellulose membranes with molecular weight cut offs of 5 kDa and 100 kDa were tested on their rejection performance towards ground corn extractants containing high concentrations of native proteins. Experimental results concerning the permeate flux decrease due to fouling and the rejection of corn proteins showed that the 5 kDa regenerated cellulose membrane was most promising.

Thompson et al. tried to recover valuable proteins directly from a corn wet milling process via micro- and ultrafiltration [144]. In the corn wet milling process, corn is steeped in water (often with sulfur dioxide addition) for about 24–36 h leading to a separation of the kernel constituents. The slurry is then separated into one stream containing highly concentrated starch and a second stream containing mostly proteins. This stream is called light gluten. It is concentrated to heavy gluten by centrifugation and then dried to gluten cake by vacuum belt filtration. The gluten cake can than be sold as corn gluten meal in animal feed. The authors used ceramic tubular microfiltration membranes (1) to concentrate the light gluten for replacing the centrifugation and (2) to concentrate the heavy gluten for replacing the vacuum belt filtration. In both processes the separation sharpness between valuable dry matter (proteins) and water is decisive for the choice of unit operation. It was found that in processing of light gluten the membrane process could compete with the centrifugation without offering an advantage in terms of product quality. In processing of heavy gluten, the membrane separation did not reach the concentration factors of the vacuum belt filtration. Nevertheless, the membrane separation allowed for the removal of undesired compounds from the gluten such as ashes or inorganics. Therefore, the authors concluded that micro- and ultrafiltration could be used to improve the product quality.

A new option to produce biofuel from biomass is to utilize (micro-) algae or other oceanic resources such as aquatic fungi. The algae/fungi are utilized the same way as conventional enzymatic systems to produce valuable intermediates for biofuel production (e.g. triacylglycerides). Algae harvesting is performed by feeding nutrients phosphate, nitrogen and optional CO_2 [145]. The recovery of produced biodiesel with simultaneous rejection of algae can be performed in a membrane bioreactor (MBR). In comparison to conventional MBRs (operating with yeasts) the algae are more likely to attach on the membrane surface and to cause fouling. Hence, specific measures have to be taken to avoid these problems, for instance by cleaning the membrane surface via pulsed backflushing [146]. Rios et al. tested polymeric and ceramic microfiltration membranes for the recovery of the microalgae strain *Phaeodactylum tricornutum* [146]. These algae produce lipids which can be transesterficated like the canola oil discussed in Section 3.1. Special scope of this publication was set on the

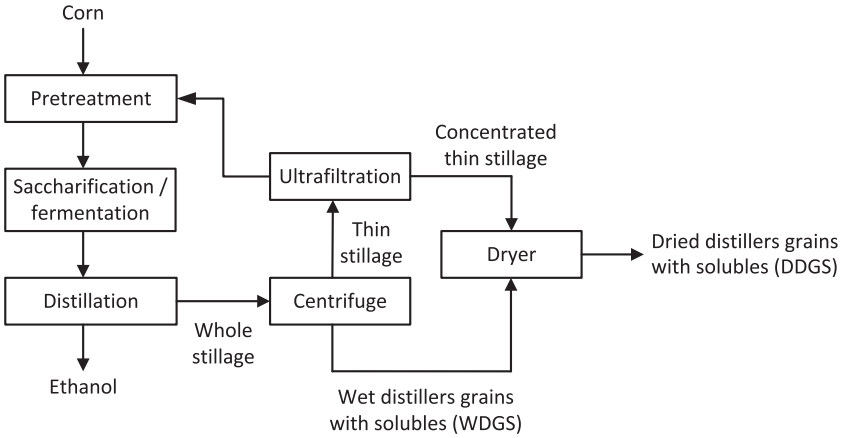

Fig. 11. Ultrafiltration process scheme for the recovery of thin stillage [137].

permeate flux reduction during short operation times. To minimize the occurrence of membrane fouling a backpulse device was used to backflush some of the filtered product solution several times per seconds in order to clean the membrane surface. In total, four different membrane modules with polymeric membranes (Teflon) and ceramic membranes (AlO_2) with pore sizes ranging from 0.5 μm to 2 μm were tested. A strong flux decline for all membranes at varying backpulse intervals of up to 1000 pulses per minute was found within the first 20 min of operation, indicating a very strong affinity of the microalgae to the membrane surface. The ceramic membranes showed a somewhat better permeate flux development than the polymeric membranes.

Similar results were obtained by Zhang et al. [147]. They recovered two marine microalgae (*Haslea ostrearia* and *Skeletonema costatum*) with a polyvinylchloride (PVC) ultrafiltration membrane module. Again, the permeate flux for these systems dropped dramatically within the first 20 min. After this time a conventional backwashing cycle was run in order to restore the initial value. As well chemical cleaning with NaOH, citric acid, or NaClO was tested to restore the initial permeability of the fouled membranes. Chemical cleaning was performed after about 10 h of operation when the permeability could be restored to just 60% of the initial value via backflushing. The best flux recovery (of 98% of the initial value) was obtained by using a 400 mg L^{-1} NaClO solution. Therefore, the authors concluded that it is possible to run such a system for longer terms.

3.4. Hydrolysis processes

Lignocellulosic raw material has to be hydrolyzed before it is fed to a fermentation broth in order to release fermentable sugars. One possibility is to separate the cellulose, hemicellulose and lignin fraction first and then to hydrolyze the cellulose and hemicellulose to glucose, respectively xylose. Such hydrolysis processes can be performed very effectively by enzymes. Another possibility is the thermal/chemical hydrolysis of lignocellulosic raw material for instance with sulfite acid. In such a process furans, phenols and carboxylic acids originate beside fermentable saccharides. In both process options membranes can enhance the pretreatment process by purifying the hydrolysate with respect to the saccharide fraction. In the following, first pressure-driven membrane operations in the enzymatic degradation of cellulose/hemicellulose will be discussed, then membrane operations in the thermal/chemical pretreatment of lignocellulosic raw material.

Cellulose stemming from wooden biomass can be converted to glucose—a common nutrient for fermentation broths—via enzymatic hydrolysis. During hydrolysis the linear polysaccharide cellulose is successively depolymerized to glucose by diverse cellulases, for instance *endoglucanases*, *exoglucanases* and *β-glucosidase*. In a batch hydrolysis of cellulose the conversion rate is often limited by product inhibition caused by cellobiose and glucose [148]. Hence, several studies deal with the recovery of glucose (and residual cellobiose) during the enzymatic hydrolysis to increase the reaction speed and the conversion rate. Fig. 12 depicts the principle of glucose recovery from an enzymatic hydrolysis of cellulose via ultrafiltration.

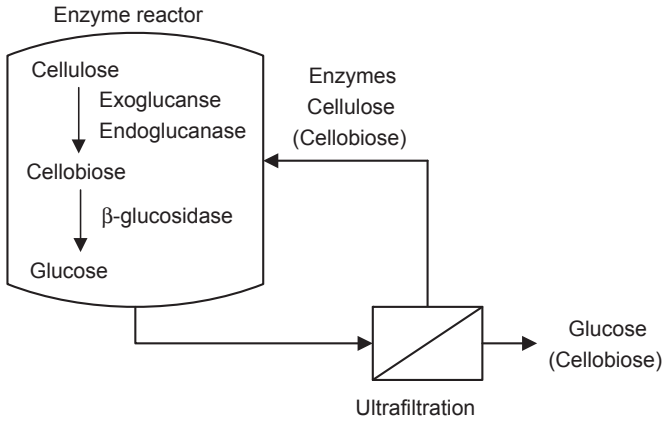

Fig. 12. Principle of glucose removal during the enzymatic hydrolysis of cellulose to decrease product inhibition of the enzymes.

Henley et al. studied the enzymatic saccharification of cellulose in a continuous stirred-tank reactor (CSTR) coupled with an ultrafiltration membrane module [149]. Initially, four different pretreated feeds were tested for their hydrolysability in batch mode without membrane filtration—sugar cane bagasse, sorghum stubble, peanut shells and—as reference—powdered cellulose. The substrates were processed with *Trichoderma viride* cellulase SP122 at a temperature of 50 °C in an acetate buffer (pH 4.8). The hydrolysis was carried out with an initial concentration of 0.45 g L^{-1} of dry substrate and 0.77 g L^{-1} of the enzyme. A conversion of about 70% was achieved using powdered cellulose as substrate. The native substrates all performed worse with conversions down to 20% in case of the peanut shells. The authors suggested that additional constituents from the native substrates, oil for instance, inhibited the enzyme activity. Then a hydrolysis of powdered cellulose was carried out with an integrated external ultrafiltration module. The employed ultrafiltration membrane provided a MWCO of 50 kDa. According to the MWCO hydrolysis products were assumed to pass the membrane while the cellulases and unreacted cellulose were preferably retained. The fluid volume in the reactor was kept constant by continuous addition of fresh nutrient solution. The hydrolysis process with continuous removal of products allowed for a conversion of up to 90%.

Alfani et al. investigated the effect of product inhibition during enzymatic hydrolysis of cellulose in a membrane reactor [150]. The investigated system comprised microcrystalline cellulose, a cellulase complex produced by *T. viride* and β-*glucosidase*. The cellulase complex hydrolyzed the cellulose as long as the cellulose chain was longer than the dimer cellobiose. The cellobiose was then converted to glucose by β-*glucosidase*. Both reactions were found to be product-inhibiting. Therefore, the authors set up a membrane reactor with an ultrafiltration membrane (MWCO was 10 kDa) to study the impact of product inhibition. An enzymatic hydrolysis in a membrane reactor was conducted, using 0.1 g L^{-1} of substrate and 0.033 g L^{-1} of the enzyme complex. In the first experiment with a low permeate flux a conversion rate of about 2% was reached after 25 h. In the second experiment the permeate flux was increased yielding an increase of conversion rate to about 5% which was the plateau. In the third experiment with the highest permeate flux the conversion rate decreased again. The increasing conversion rate with increasing permeate flux was explained by enhanced removal of inhibiting glucose, while the subsequent decrease was explained with an accumulation of enzymes at the membrane surface which were then unable to process the insoluble cellulose.

Ohlson et al. investigated the enzymatic hydrolysis of pretreated sallow with and without subsequent washing [151]. In both experiments the substrate was pretreated with a hammer mill and 4 wt% of NaOH. In the first experiment the substrate was directly diluted to 100 g L^{-1} in a 0.1 M acetate buffer solution (pH 4.8). In the second experiment the substrate was washed with pure water to remove residual NaOH prior dilution. Then both substrate slurrys were hydrolyzed with cellulases obtained from *Trichoderma reesei*. A comparison revealed that subsequent washing of the pretreated substrate resulted in an increased conversion rate. Then the influence of agitation speed on enzyme performance was investigated with the result that the enzyme activity

was not affected for agitation speeds of up to 500 rpm. However, a conversion rate of just 40% was reached in the conventional batch reactor within 20 h. Thus, an UF membrane providing a MWCO of 10 kDa was used to separate the product inhibiting glucose from the residual sallow substrate during hydrolysis. In result the conversion rate increased significantly to 95%.

Kinoshita et al. also studied an ultrafiltration membrane reactor for the enzymatic conversion of carboxymethylcellulose [152]. They utilized cellulases of *Sporotrichum cellulophilum* to produce glucose. The hydrolysis was performed within 120 h with an initial substrate concentration of 100 g L^{-1} and an enzyme concentration of up to 20 g L^{-1} in a sodium acetate buffer solution (pH 5.5). Fresh substrate was added to the solution as soon as half of the present substrate had been hydrolyzed. The authors tested the enzymes on product inhibition with the result that 1 wt% of cellobiose caused a decrease in activity of 60% and 1 wt% of glucose of 40%. The membrane reactor was then operated with different permeate flow rates. With increasing flow rates of up to 15 mL h^{-1}, more glucose could be collected. After about 40 h of operation the productivity decreased significantly. The authors proved that the deactivation of the enzymes could not be induced from leakage. An irreversible binding of the enzymes on the insoluble cellulose was also excluded. In addition, the effect of operation temperature was investigated with the result that a temperature of 37 °C during operation was too low for a deactivation of the enzymes. In fact, the productivity could be maintained for temperatures of up to 60 °C. Finally, the reason for enzyme deactivation was found in the presence of proteases which were present in the crude enzyme.

Belafi-Bako et al. operated a tubular membrane reactor to study cellulose hydrolysis with a commercial enzyme preparation produced from *T. reesei* [153]. The reaction was carried out at 50 °C and a pH of 4.8 maintained by sodium acetate buffer. Two different membranes were tested regarding their separation performance for glucose — a porous stainless steel tube covered by a non-woven textile layer (Fiteving 500N) and a flat sheet module with a Nadir 30 membrane providing a MWCO of 30 kDa. A conversion rate of 53% was obtained for this system. The authors concluded that the membranes were able to retain the enzymes and permeate the inhibitory products. The comparable low conversion rate was explained with a certain amount of the intermediate product cellobiose which could have left the reactor without being completely converted to glucose.

Gan et al. set up an integrated membrane reactor to study the enzymatic degradation of α-cellulose, obtained from hardwood pulp by bleaching and pulverizing [154]. The system comprised a reaction vessel with a holding volume of maximum 2.5 L and an ultrafiltration membrane providing a MWCO of 10 kDa. The hydrolysis was carried out with enzymes from *T. reesei* at a reaction temperature of 40 °C and a pH of 4.7, maintained by sodium acetate buffer. The cellulose concentration was set to 25 g L^{-1} and the enzyme concentration to 100 mg L^{-1}. Three different operation modi were tested with the system: (1) a common batch hydrolysis, (2) a semi-continuous operation with intermittent filtration of the products and (3) a continuous operation with constant permeate flux. A typical flux of 7.0–9.0 L m^{-2} h^{-1} was set up. During filtration a strong permeate flux decline was observed within the first 5 h at a total operation time of 50 h. To recover the initial permeate flux, an electrical cathode in form of a stainless steel mesh was placed underneath the membrane and two anodes in form of electric wires were placed 1 mm above the membrane surface. Then the system was charged up with electric backpulses at 300 V, resulting in the ejection of negatively charged molecules and substrates from the membrane surface. Best results were obtained for the continuous mode with a product yield of 53% in comparison to 35% in batch operation. The limited increase in total performance was explained by low product inhibition due to low enzyme concentrations of 10 g L^{-1} and 30 g L^{-1}.

Mores et al. studied the recovery of enzymes – cellulases — during hydrolysis of lignocellulosic particles (which were not specified in detail) via micro-and ultrafiltration [155]. Here, a cross-flow module was operated (see Fig. 13). Prior to the ultrafiltration the aqueous mixture consisting of lignocellulosic material and cellulases was processed in a sedimentation tank and a dead-end microfiltration test cell in order to remove the larger particulates. The cross-flow apparatus was equipped with a backwash unit to minimize the fouling potential for the employed membrane. A comparison between initial permeate fluxes and permeate fluxes after one hour of continuous operation showed that the permeate flux dropped from initially 15,000 LMH (Liter per square Meter and Hour) during the first 20 min. Afterwards it remained stable at a value of about 400 LMH for a mixture containing 0.2% w/v of lignocellulose and 0.3% w/v of cellulase. This phenomenon was attributed to initial fouling. After a 5 min backwash cycle the initial permeability was restored as far as possible with a value of 11,000 LMH. A cost analysis revealed that a membrane based recovery of cellulases with an average permeate flux of about 20 LMH allowed for cost savings in comparison of a complete replacement of cellulases. Hereby it was assumed that 75% of the cellulases were still alive after recovery.

Knutsen from the same research group extended the prior work by analyzing the enzyme activity in the above described system

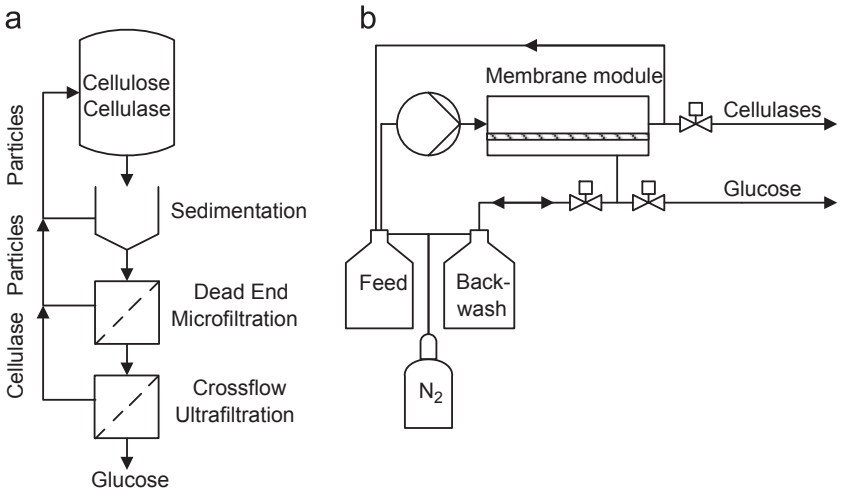

Fig. 13. (a) Process scheme for recovery of cellulase and (b) scheme of the ultrafiltration membrane cross-flow filtration apparatus for separation of cellulase from lignocellulosic particles [155].

[156]. For a system containing 0.22 g L^{-1} cellulase and 10 wt% lignocellulose a permeate flux of 90 LMH (with the sedimentation tank as bottleneck) could be reached and the enzyme activity remained constant within the accuracy of measurement.

Sjöman et al. studied the xylose recovery of hemicellulose hydrolysates via nanofiltration [157]. Three different nanofiltration membranes, namely the Desal DL, Desal DK and NF270 membrane were tested on their separation performance regarding xylose in mixture with hemicellulose hydrolysate. The feed pressure was varied between 20 bar and 40 bar and the temperature was varied between 40 °C and 60 °C. Further long term studies were carried out to evaluate the effect of fouling on the membrane performance. The overall permeate flux and the xylose flux increased by increasing the temperature, respectively the pressure. However, the selectivity between xylose and glucose, which is a side-product in this case, was found to be rather low and even decreased with increasing filtration temperature. Nevertheless, the authors concluded that for sugar purification nanofiltration membranes could replace high performance separation techniques such as chromatography.

In a recent overview, Andric et al. discussed the optimal design of a membrane reactor with respect to yet published results [158]. One suggestion to run such a reactor effectively was to use relatively large reactor volumes with a comparable small separation system to allow for a fast removal of glucose and to keep the initial product formation rate high. Such a system was assumed to work effectively at glucose concentrations not higher than 10 g L^{-1}. In order to allow for a stable long-term operation of the membrane reactor, an enzyme concentration not higher than the critical limit of 10 FPU/$g_{cellulose}$ (FPU — Measurement of total enzyme activity) was suggested. Otherwise the additional enzymes would be washed out of the system. Following unresolved questions and problems needed to be addressed from the author's point of view (1) to avoid low product concentrations, the glucose level had to be increased in the reactor, (2) to ensure a long-term stable operation, minimization of membrane fouling had to be addressed, especially at high substrate concentrations and (3) in addition the feasibility of a scale-up had to be proven.

Lignocellulosic raw material cannot just be enzymatically hydrolyzed, but by thermal/chemical pretreatment as well (see Section 2.5). In such a process scheme several side-products originate from the raw material such as furans, phenols and carboxylic acids. Especially furfural is not just toxic for fermentation broths, but is a valuable chemical itself. Hence, its defined separation and recovery from hydrolysates containing saccharides as main product is of high interest. Luo et al. investigated the separation of furfural from hydrolysate model solutions via nanofiltration [159]. The authors tested the NF90 and NF270 nanofiltration membranes from DOW on their separation performance regarding saccharides/furfural from model solutions. Due to the different molecular weights of the saccharides (150–180 Da) and furfural (96 Da) the saccharides were mainly rejected while the furfural passed the membrane. The tighter NF90 allowed for a complete rejection of saccharides (99%) with partial rejection of furfural between 20% and 40% depending on the feed pressure which was varied between 6 and 20 bar. The NF270 allowed for a complete permeation of furfural, but showed lower rejections of the saccharides between 60% and 90%. The authors concluded that nanofiltration could be used to first concentrate the saccharides by operating the NF90 and then to remove the furfural by operating the NF270 membrane.

Maiti et al. also studied the separation of side-products from a lignocellulose hydrolysate via nanofiltration [160]. They processed rice straw hydrolysate with diverse polyamide membranes provided by Permeonics and a polyethersulfone membrane provided by NovaSep with MWCOs ranging from 100 Da to 400 Da. They were tested on their separation ability for several compounds from the hydrolysate such as glucose, xylose, fructose and cellobiose which are the sugar fraction and acetic acid, ferulic acid, furfural, HMF and vanilic acid which are the side-product fraction. The experimental results showed that it was possible to separate the sugar fraction efficiently from the side-product fraction by employing a 150 Da membrane.

A similar study concerning the separation of furans and carboxylic acids from a hyrolysate via nanofiltration was published by Weng et al. [161]. The Desal DK from GE Osmonics providing a MWCO of 150–300 Da was used to filter rice straw hydrolysates. Aim was to separate acetic acid, furfural, HMF and formic acid from the sugar fraction comprising xylose, glucose and arabinose. The membrane allowed for a rejection of saccharides from 80% to 100% while the side-products passed the membrane without significant rejection. For furfural, formic acid and HMF even negative rejections were measured which means that these substances were concentrated in the permeate. An increase of operating temperature from 25 °C to 40 °C resulted in a slight decrease of saccharide rejection. This was explained by an opening of the membranes pores which allowed an easier passage of the saccharide molecules.

In summary, we conclude that membrane technology can enhance the enzymatic conversion of cellulose to glucose. Nevertheless, the exact increase in productivity can hardly be predicted due to the diversity of physical phenomena which play a role and are not fully understood yet. These physical phenomena include coupling between reaction kinetics of the cellulose hydrolysis and product removal or the influence of concentration polarization on the membrane performance. Eventually, a safe scale-up to a technical apparatus, such as a membrane bio-reactor (MBR) can be performed. Furthermore, published studies just focused on the glucose recovery from an enzymatic hydrolysis as stand-alone process. Future research has to address the implementation of cellulose hydrolysis to glucose into a biorefining process such as fermentation. Here, it has to be proven that membrane separations allow for a cost-efficient improvement of the (ligno-) cellulose hydrolysis in terms of product recovery and quality with significant effect on the following fermentation process.

In the thermal/chemical hydrolysis of lignocellulosic raw material membrane technology can be employed to separate the diverse compounds originating in the hydrolysis process. Aim is on the one hand to purify the saccharide fraction of the hydrolysate for an efficient fermentation and on the other hand to separate the valuable side-products from the hydrolysate. Here, a detailed fractionation process adapted to the respective raw material has to be set up to allow for a complete utilization of the biomass constituents with respect to their commercial benefit.

3.5. Solvent recycling based biorefinery

Processing of lignin-rich biomass is sophisticated, due to the strong binding of the lignocellulose which can hardly be disintegrated. Hence, disintegration of such biomass is performed with aggressive solvents. Two commercial processes have yet been established comprising the treatment of wooden biomaterial with strong solvents: (1) the Kraft process (see Figs. 14 and 2) the Organosolv process (see Fig. 15).

The Kraft process is a large-scale industrial process established in the pulp- and paper-industry for recovery of cellulose for the paper production. Within the process wood chips are initially impregnated with white liquor which is a mixture of sodium hydroxide and sodium sulfide in aqueous solution. Then the impregnated chips are processed in a digester for several hours at temperatures of about 170 °C, where they decompose to a chemical pulp containing mostly cellulose and the lignin and hemicellulose fragments which are

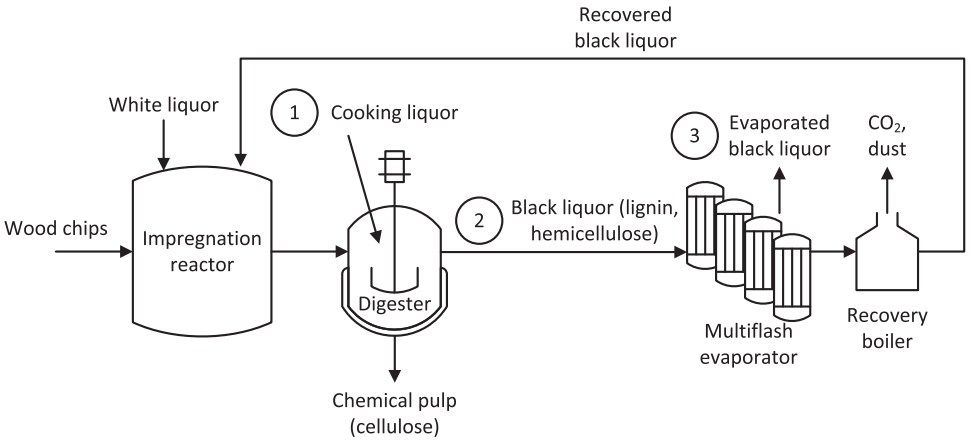

Fig. 14. Simplified process scheme of the Kraft process. Numbers indicate possible applications for ultra- and nanofiltration membranes for lignin recovery from cooking liquor, respectively black liquor.

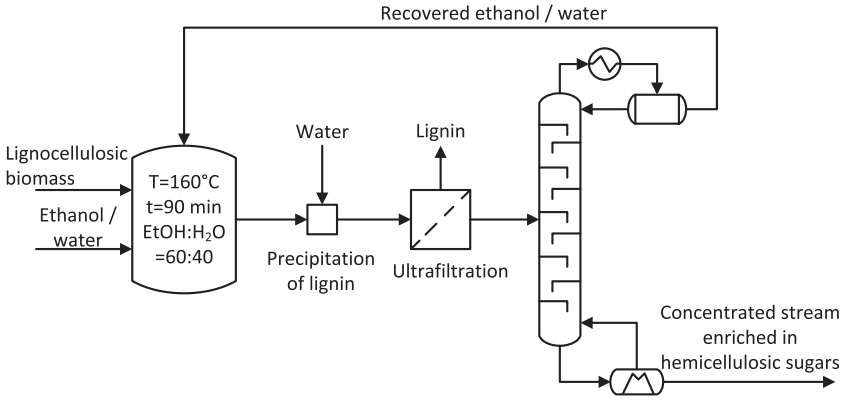

Fig. 15. Simplified process scheme of the Organosolv process with integrated ultrafiltration [175].

dissolved in the liquor. This so-called black liquor is then processed by multi-flash evaporation for concentration of the solids which can than be burned in a recovery boiler. The recovered black liquor is recycled to the impregnation reactor.

As lignin is nowadays considered as valuable chemical, its recovery from cooking liquor, respectively black liquor promises a commercial benefit in comparison to energy generation by burning [162]. Ultra- and nanofiltration membranes were investigated for the separation of lignin from the diverse process streams shown in Fig. 14.

Wallberg et al. investigated the recovery of lignin directly from the digester containing only cooking liquor [163]. Due to high temperatures above 100 °C, ceramic membranes were chosen for this application. Kraft cooking liquor from a paper production plant was directly fed to the membrane pilot plant. Typical parameters such as trans-membrane pressure, cross-flow velocity and the temperature were varied during operation. A recovery of 20–30% of lignin from the liquor was reached. Toledano et al. investigated the possibility to recover lignin from black liquor downstream of the digester [164,165]. Here, the fluid temperature is somewhat lower than in the digester itself — about 90°C — but still so high, that only ceramic membranes were applied in the studies. In this case, the employed membrane was able to separate different fractions of lignin ranging between 1000 Da and 100,000 Da. The authors concluded that sharpening the quality of lignin could encourage its commercialization as stand-alone product. In addition, the ultrafiltration process was superior to the conventional precipitation process, because the obtained lignin fraction had lower molecular weights and was less contaminated.

Cold black liquor solutions were processed with polymeric ultrafiltration membranes by Satyanarayana et al. [166]. Here, fouling problems occurred during filtering black liquor solutions through cellulose acetate membranes placed different module geometries (radial, rectangular and stirred). A flux decline due to increasing cake layer on the membrane surface and osmotic pressure was found for all tested set-ups, whereas usage of the stirred cell set-up was beneficial for the flux and rejection of contaminants. Liu et al. also processed cold black liquor solutions with inorganic membranes in order to separate the lignin fraction from the cellulose fraction [167]. They observed membrane fouling as well and investigated the possibility of long-term runs (over 1000 h) with back-wash cycles repeated every 30 min. They observed a lignin separation from the black liquor of up to 90%. Dafinov et al. studied the filterability of cold black liquor via ceramic ultrafiltration membranes [168]. They found that the volume of spent liquor could be reduced to about half by applying ultrafiltration, but observed a strong flux decrease due to the formation of a gel layer on the membrane surface. Schlesinger et al. [169] studied nanofiltration membranes to recover hemicellulose from cold black liquor. They proved that hemicellulose could be effectively separated from sodium hydroxide — a constituent of the liquor — by alkali resistant nanofiltration membranes. Colyar investigated the possibilities to fractionate and separate lignin compounds from caustic chemicals [170]. It was possible to fractionate these compounds, although a strong flux decline due to an appearing gel layer was observed.

Restolho et al. used ultrafiltration, nanofiltration and reverse osmosis membranes to remove any particulates and impurities from spent liquor successively [171]. In this publication samples of thin spent sulfite liquor were taken from the first stage of a multi-evaporation plant. Several membranes were investigated for the

ability to purify the solvent after evaporation. Experimental results showed, that it was possible to reject the lignocellulosic material, even the sugar fraction to values of about 95% by applying reverse osmosis membranes. The second aim, fractionation of the lignosulfates or separation from the oligomeric sugars was not reached due to an overlap of the molecular weights. Falth et al. studied the purification of spent liquor by application of polymeric ultrafiltration membranes [172]. The authors found, that it was not just possible to remove the organic compounds from the solvents, but also to remove some inorganic solutes which usually can pass the membrane easily. The authors concluded that especially multivalent ions salts coordinated with the large organic compounds and were retained with them.

Afonso extended this work with a further publication on acetic acid and furfural recovery from spent liquor via nanofiltration and reverse osmosis [88]. The liquor was collected from the top of the first evaporator of a battery of seven evaporators (see number 3 in Fig. 14). It contained residuals from the pulping of *Eucalyptus globulus*, namely acetic acid, furfural and lignosulphates. Diverse reverse osmsosis membranes (e.g. RO99 and DSS-HR98PP from Alfa Laval) and nanofiltration membranes (e.g. NP030/NP010 from Microdyn Nadir and NF200/NF270 from Dow Filmtec) were tested regarding their separation performance for these residuals. As expected, the reverse osmosis membranes allowed for the best separation performance of about 90% for all three substances. The nanofiltration membranes performed worse but still offered retentions of about 60% for Furfural, 40% for the lignosulphates and about 20% for the acetic acid.

Jonsson et al. studied the treatability of spent liquor (in this case black liquor) prior and after the evaporation stage via membrane filtration as well [173]. The authors aimed for a recovery of lignin from black liquor and compared two possible processes: (1) ultrafiltration of black liquor withdrawn from the evaporation stage, (2) ultra- and nanofiltration of black liquor prior the evaporation stage. A cost analysis concluded that both processes imposed similar costs. However, the lignin concentration and purity in the combined ultra- and nanofiltration process was superior to the single ultrafiltration after evaporation.

Werhan et al. studied the separation of lignin from ethylacetate solvents via nanofiltration [174]. In their work they first conducted an oxidation of Kraft lignin from pine. The lignin oxidation products comprising mainly monomers, dimers and trimers were then extracted with ethyl acetate. Several solvent resistant nanofiltration membranes where then tested on their separation performance of lignin monomers from lignin polymers. The commercial Duramem™ 900 membrane showed the best performance regarding the permeate flux with a value of 100 L m^{-2} h^{-1} bar^{-1}. Taking the separation results into account the authors concluded, that the Puramem™ S380 membrane gave most satisfying results, due the fastest removal of the monomeric lignin products from the feed solution with simultaneously high rejection of polymeric products of 71.1%.

The Organosolv process was patented in 1971 (US Patent 3,585,104) and was originally set up for the production of ethanol from wooden biomass. Its process scheme is shown in Fig. 15. In the Organosolv process, lignocellulosic material is dissolved in an ethanol/water mixture. Here, membrane technology is employed to purify the solvent in terms of lignin removal as well.

In a recent publication, Alrios and Garcia studied an ultrafiltration unit operation within the Organosolv process to extract wood constituents from the spent solvent [176]. They performed process simulations to estimate the production costs of such obtained lignin. They assumed that the ultrafiltration membranes could separate the liquid fraction from the reactor into four fractions containing solutes with molecular weights between 5 kDa and 15 kDa. Such ultrafiltration membranes would allow for a fractionation of low and high molecular weight lignin comparable to lignin obtained from the Kraft process. Process costs were estimated to 52€/ton of lignin. In a further publication, Garcia et al. compared the Organosolv process (with integrated ultrafiltration) with the soda process in terms of costs by performing a process simulation [175]. The optimum flow sheet for the Organosolv process included the membrane based separation of lignin shown in Fig. 15.

Egüés et al. investigated the separation and purification of hemicellulose by ultrafiltration downstream of an auto-hydrolysis process for corn wastes [177]. The raw material was heated to a temperature of 180 °C for 30 min at solid to liquid ratio of 1:20. For the filtration experiments, ceramic membranes providing MWCOs of 1, 5 and 10 kDa were chosen. The auto-hydrolysis liquor was filtered successively yielding four fractions: <1 kDa, <5 kDa, <10 kDa and >10 kDa. Afterwards ethanol was added to each fraction to precipitate the hemicellulose. Subsequently, diverse analytical techniques, such as GPC, FT-IR, TGA, H NMR and CHNS-O spectrometry were applied to analyze the precipitated hemicellulose. Results showed, that the fraction <10 kDa contained most of the hemi-cellulosic sugars and other organic matter.

4. Electrical-driven membrane processes

4.1. Organic acid recovery from fermentation broths

Electrodialysis (ED) processes benefit from their large variety of membrane configurations which allow for an implementation in several processes related to biomass conversion. A very large field is the recovery of valuable organic acids from fermentation broths. Here, several electrodialysis stack configurations, such as monopolar electrodialysis or electrodialysis with bipolar membranes are applied to recover or concentrate the respective acid from the fermentation broth. Huang et al. published a comprehensive overview of ED application in organic acid production and discussed the several stack configurations in detail [178]. For the recovery of organic acids from a fermentation broth the most common stack configuration is the conventional electrodialysis (CED) which comprises alternating anion exchange membranes (AEM) and cation exchange membranes (CEM). A variant of such a stack configuration is shown in Fig. 16.

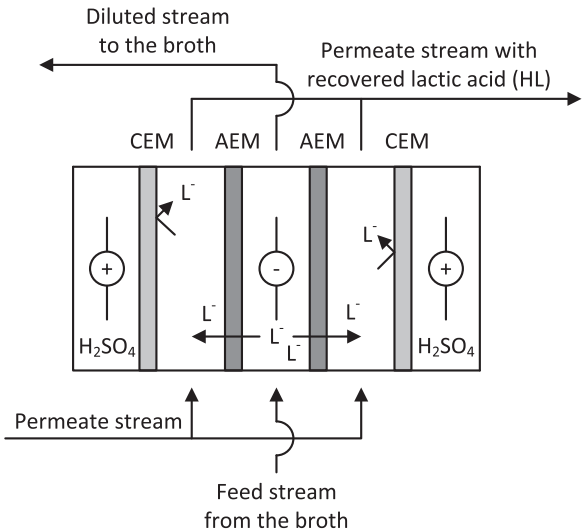

Fig. 16. Conventional electrodialysis system (CED) for the direct recovery of lactic acid from a fermentation broth [179]. AEM—anion exchange membrane; CEM—cation exchange membrane.

In this configuration the fermentation broth is directly led through the middle chamber of the stack which is surrounded by anion exchange membranes. The negatively charged lactic ions can pass the membrane and concentrate in the permeate stream. The retentate stream is depleted by lactic ions and can be redirected to the fermentation broth. For control of the pH value of the fermentation broth this ED set-up has to be run intermittently: The fermentation has to be run for a certain time, until the pH value drops due to the produced acid to a yet tolerable value. Then the electrodialysis process has to be started for removal of produced acid from the broth until the pH value is high enough for further acid production in the fermentation broth.

The conventional process for a batch-wise production of organic acid out of a fermentation broth is the precipitation of organic acid from the broth by adding a neutralizing base after the fermentation, for instance caustic soda. The precipitated salt can than be removed from the fermentation sludge by filtration. Electrodialysis with bipolar membranes (EDBM) simplifies this process scheme by continuous removal of salt from the fermentation broth which is transformed to an organic acid during electrodialysis. A simplified scheme of an EDBM process is shown in Fig. 17.

In comparison to the conventional electrodialysis, utilizing exclusively cation and anion exchange membranes, the stack is extended with two bipolar membranes which are usually placed next to the electrode chambers and split water molecules. H^+ and OH^- ions are produced in the interface of the laminate of cation and anion exchange membranes. The feed stream with the particular salt is led through the middle chamber which is surrounded by an AEM and a CEM membrane. The salt is split up, with the cation moving through the CEM and the anion moving through the AEM.

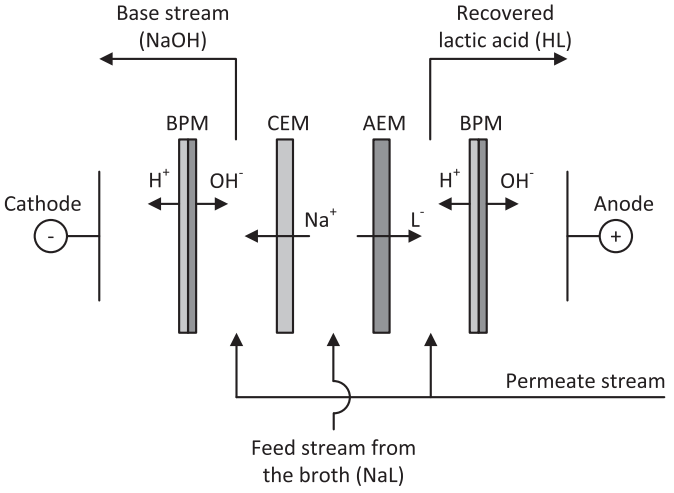

Fig. 17. Electrodialysis with bipolar membranes (EDBM) for the recovery of organic acids from organic salts. BPM—bipolar membrane.

In the respective neighbor chambers the separated ions are combined with the respective H^+ ions and OH^- ions, stemming from the water splitting membrane to form the respective base and acid. Simply articulated, the EDBM enables the separation of salts into the respective base and acid.

Another possibility to split an organic salt into base and acid is the so-called ion substitution electrodialysis (ISED) which is presented in Fig. 18. Here only one type of ion exchange membrane is employed, in this example a cation exchange membrane. The organic salt is fed alternatingly with an acid stream to the compartments of the stack. As only cations can move within this configuration the cation of the salt and the H+ ion of the acid are transported to the neighbor chambers and form conversely a salt and an acid. Simply spoken the organic salt is converted to an organic acid, while a replace acid is transformed to a salt (of lower value).

The most investigated organic acid recovery process is the one for lactic acid, because lactic acid is already industrial produced in very large quantities. In the fermentation broth the produced lactic acid causes product inhibition due to a decrease in pH. In the conventional fermentative production of lactic acid the pH is controlled via addition of ammonium, sodium or calcium to form the respective salt. This procedure includes the drawback of solidification of the fermentation broth due to a low salt solubility what results in a complicated downstream processing for refining lactic acid. Thus, several studies on the downstream recovery of lactic acid via electrodialysis were presented applying different ED operation modi. The lactate can form an acid or a salt, depending on the pH value of the solution and present ions.

Hongo et al. implemented electrodialysis in the production of lactic acid from a *Lactobacillus delbrueckii* fermentation broth already in 1986 [179]. They used a conventional electrodialysis (CED) set-up to recover lactic acid. The set-up comprised a controller which allowed the automatic start-up of the electrodialysis process, when the pH dropped under a certain value and to shut-down the electrodialysis process after a certain time, when the pH was restored to a value of 5.5 again which was found to be optimal for the fermentation process. The concentration of lactic acid in the broth could be maximized from formerly 1 wt% without

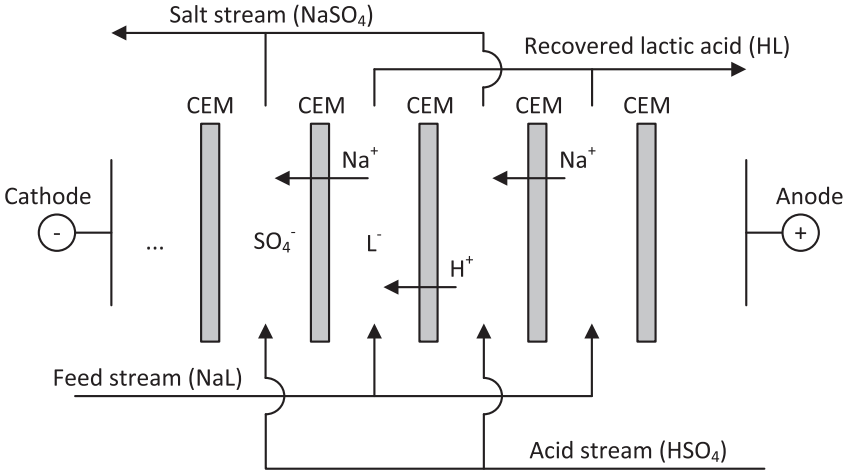

Fig. 18. Principle scheme of an ion substitution electrodialysis (ISED) [180].

pH control to about 5 wt%. During operation of the ED, lactic acid could be recovered from the broth as pure solution which is an advantage to the conventional method of neutralizing the produced lactic acid to the respective salt which solidifies in the broth.

Nomura et al. published studies in which they compared batch fermentations without pH control, pH control by adding neutralizing salt $CaCO_3$ and pH control by removal of lactic acid via ED [181]. The investigated system comprised a fermentation broth of *Lactobacillus delbrueckii* and an ED setup with alternating anion exchange membranes and cation exchange membranes. To minimize fouling of the membranes by the microbial cells in the fermentation broth, the cells were immobilized in a calcium alginate bead. To stabilize the cells in the calcium alginate bead, 10 mM $CaCl_2$ was added to the fermentation broth. Then a semi-continuous production of lactic acid was conducted with fermentation cycles of 5 days. Within 5 days, the lactic acid concentration in the fermentation broth raised to 10 g L^{-1} when the pH was not controlled. By controlling the pH of the broth via addition of the neutralizing salt $CaCO_3$ the lactic acid concentration in the broth could be increased to 50 g L^{-1}. For the pH controlled system with ED an even higher value of 70 g L^{-1} was reached. Therefore, the productivity of the fermentative system could be maximized by recovery of lactic acid via ED.

Wang et al. also investigated the recovery of lactate from a fermentation broth via conventional electrodialysis [182]. In contrast to the other publications, the authors did not use glucose to feed the broth, but kitchen garbage. An analysis of the garbage showed that it contained up to 95% of organic components, stemming from rise, bread, vegetables and fruits. For the fermentation *Lactobacillus* was used and for the recovery of lactic acid a conventional electrodialysis stack was set up. After a batch fermentation ammonia lactate was recovered as lactic acid, while ammonia sulfate remained as side-product. The authors could recover about 90% of lactic acid from the broth with an average current efficiency of 93%.

Choi et al. investigated an ion substitution electrodialysis (ISED) process for the recovery of lactic acid from sodium lactate [180]. In this process only cation exchange membranes were implemented allowing exclusively protons to move from one compartment to the other. The ED stack compartments were alternately fed with the sodium lactate feed stream and a sulfuric acid stream for ion substitution. The outgoing streams were then lactic acid and sodium sulfate (see Fig. 18). The authors compared this configuration with a CED configuration which was alternately fed with a sodium lactate and a sulfuric acid stream as well. In the CED process a considerable loss of lactic acid was observed, because the lactate did not remain neutral during operation, but was ionized. Hence, it was transported through the anion-exchange membrane. During the ISED this effect was not observed, because there were no anion-exchange membranes present in the configuration which allowed the movement from lactate to the neighbor compartment. Therefore, they concluded that the ISED is advantageous in comparison to the CED process.

A similar concept for the recovery of lactic acid from sodium lactate via ED was presented by Kim and Moon [183]. In contrast to Choi the authors used caustic soda as additional feed stream for the ED stack to convert the sodium lactate into lactic acid. By using bipolar membranes which provided H^+ and OH^- ions the authors achieved the production of lactic acid without simultaneously producing a salt as (undesired) side-product. In principle, the sodium lactate stemming from the fermentation broth was split up into lactic acid and caustic soda. The authors tested two different stack configurations – one configuration with one anion exchange membrane between the two middle compartments and one configuration with an additional cation exchange membrane and compartment. For the two-compartment configuration the authors obtained a lactic acid recovery of 73.9%, while for the three-compartment configuration a recovery of up to 98.7% could be obtained. In addition, the current efficiency of the two-compartment configuration was significantly lower (17.8%) than for the three-compartment configuration (83.0%). In summary, the authors suggested to use the three-compartment configuration because of the better efficiency and the simultaneous recovery of caustic soda as separate stream which allowed for a pH control of the fermentation broth.

Bailly et al. discussed the economics of EDBM for the recovery of organic acids [184]. In their study they published detailed informations on the costs of a running EDBM plant for the recovery of lactic acid. They calculated costs of 0.47€ per kg produced acid for a production capacity of 5000 t of pure acid per year.

Habova et al. examined a two-stage ED process to recover (1) sodium lactate from a fermentation broth and (2) to convert sodium lactate to lactic acid [185]. In the first ED process sodium lactate was recovered from a fermentation broth via conventional desalting electrodialysis. The sodium lactate concentration in the recovery stream was four times that of the initial solution. The limiting current density was determined with model solutions to a value of 8.8 mA cm^{-2} at a lactate concentration of 6.5 g L^{-1}. This value was not exceeded in the experiments with the fermentation media to prevent scaling on the membranes. For the second stage the experimental set-up was extended with bipolar membranes (BPMs) to split the sodium lactate into lactic acid and sodium hydroxide. A final lactic acid concentration of up to 120 g L^{-1} in the product solution was reached.

Danner et al. studied the recovery of lactic acid from grass silages [186]. They pretreated the various silages via ultrafiltration and than purified the product stream via mono-polar electrodialysis. The energy consumption was relatively high, reaching up to 1.76 kWh kg^{-1} of transported lactate. This was explained by an undesired transport of water and minerals, such as potassium, phosphor or magnesium present in the silage. However, the ED process allowed for a concentration and purification of lactate from the various silage streams.

Min-tian et al. studied the batch-wise production of lactic acid from a fermentation broth with downstream recovery of lactic acid via conventional electrodialysis [187]. They employed *Lactobacillus rhamnosus* to produce lactic acid under anaerobic conditions. During the fermentation the broth was directly fed to the ED stack. Thus, the membranes had to be cleaned after the experiments with RO water, HCl and NaOH. The lactic acid productivity increased two-fold by adding an electrodialysis downstream process for simultaneous product removal to a batch fermentation process. An average productivity of 2.2 g L^{-1} h^{-1} was achieved during batch fermentation with ED recovery of lactic acid.

In a further publication, Min-tian et al. extended the experimental set-up with a level meter for control of the fermentation broth volume and performed long-term experiments with continuously run fermentations [188]. The electrodialysis device was operated continuously as well and the glucose concentration in the broth was set to a concentration of 175 g L^{-1} which was found to be optimal. With these conditions a productivity of 8 g L^{-1} h^{-1} of lactic acid could be achieved during over 200 h of continuous operation. In a further publication of the same group Hirata et al. optimized the set-up once more [189]. Now an on-line GC controller was implemented in the fermentation reactor for an exact control of the glucose concentration in the fermentation broth. By optimizing the set-up with this device the yield could be raised to 13.2 g L^{-1} h^{-1} with simultaneous increase of productivity.

Bailly et al. investigated the concentration of sodium lactate via conventional electrodialysis with special focus on transport phenomena of the molecules [190]. Therefore, a model was set up which involved diffusion and electro-migration of the respective

solutes. To validate the theoretical data, experiments with a synthetic solution of sodium lactate and with a clarified broth composed of ammonium lactate were performed. In a batch ED the concentration in the concentrate stream reached a maximum after a certain time even though there was still salt in the feed/diluate stream present due to a back diffusion of ions from the concentrated stream to the diluate. The authors also investigated the influence of the respective counter ion for the example of sodium lactate and ammonium lactate and found that the influence was negligible. Small differences in the volume flow were explained by a difference of the hydration number of the counter ions.

Li et al. implemented the fermentation reactor directly in an ED stack and called this device an electrokinetic bioreactor [191]. The reactor chamber was surrounded by an anion exchange membrane which allowed the transport of the lactate from the fermentation broth into the neighbor chamber (concentration chamber) and a bipolar membrane which released OH^- ions into the fermentation chamber to keep the pH constant. The pH control even allowed operating a fermentation broth at a higher pH than neutral without addition of a base. In this case a pH of 6.5 was set by an automatic pH controller which turned the power supply for the ED on and off, when necessary. A yield of 62% of lactic acid over glucose consumption was achieved.

Thang et al. also studied recovery of valuable substances such as lactic acid, but also of amino acids from grass silage juice [193]. At a pH of 6.7, the amino acids could be separated from the lactic acid and minerals. In a second step lactic acid was isolated by electrodialysis at a pH of 2.

An intricate process is the so-called reverse electro-enhanced dialysis (REED) for lactate recovery presented by Prado-Rubio et al. [192,194]. In fact, the process is considered an electro-enhanced diffusion dialysis process combined with a reverse electrodialysis add-on. A process scheme is given in Fig. 19. The authors assumed that the feed solution did not just consist of sodium lactate, but that potential fouling constituents stemming from the fermentation broth were also led through the membrane stack. The middle chamber contained the dialysate which was enriched on product while flowing through the stack. The lactate can be recovered from the fermentation broth by dialysis, but the pH of the feed could be controlled as well. In comparison to a conventional electrodialysis process a minimum configuration of only two anion exchange membranes had to be set-up. A second, more striking advantage was the avoidance of fouling on the membrane surface in long-term operation by altering the current periodically. The operation with such a stack was modeled in detail taking effects such as transient flux inversion or preferable ion transport at the membrane interfaces into account. The authors predicted a certain drop of current efficiency, depending on the frequency of current flow inversion which they could find in experiments as well.

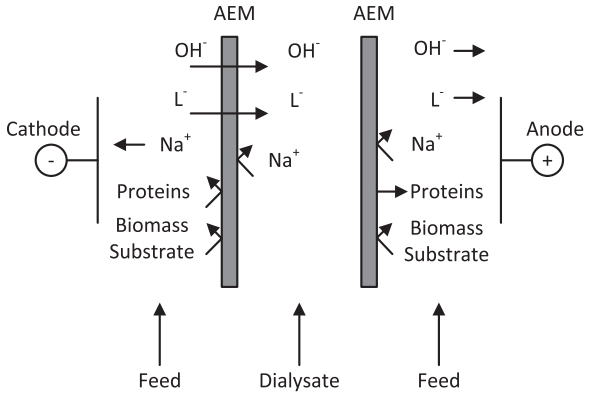

Fig. 19. Scheme of the reverse electro-enhanced dialysis (REED) for the recovery of lactic acid with avoidance of membrane fouling [192]. In this Figure the lactate (L^-) ions move from left to right. By switching the power supply, cathode and anode are reversed and the flow of ions is in opposite direction.

Akerberg et al. discussed the economy of lactic acid production from whole-wheat flour fermentation coupled with electrodialysis recovery [195]. The process flow sheet which was completely simulated with literature data which comprised the enzymatic liquefaction and saccharification of the starch, the fermentation with *Lactococcus lactis* ssp. *lactis*, the downstream separation of colloids or proteins via centrifugation and ultrafiltration from the lactic acid and finally the recovery of lactic acid via BPM electrodialysis. The authors assumed a product concentration of lactic acid of 70 wt%. The authors concluded that the recovery of residual wheat flour and proteins after the fermentation as fodder was not economic, because the costs of drying would exceed the value of the generated fodder. They also found, that an integration of the saccharification and the fermentation reduced the expected costs only slightly, due to the elimination of one reaction tank. In contrast, the simulation results showed that the recovery of sodium hydroxide, which is produced in the electrodialysis step and can be recycled to the fermentor, reduced the costs significantly. The authors suggested running the process at a rather low pH of about 4–5, because the costs of sodium hydroxide in the fermentor and in the conversion of lactate in the ED could be lowered. At last the authors recommended a batch wise production of lactic acid, because a continuous fermentation would suffer from a low product formation rate due to constant high lactic acid concentrations in the fermentation broth resulting in a strong product inhibition of the bacteria. Estimated costs were about 1.06–1.10 US$/kg produced lactic acid, depending on the wheat flour concentration. The ED recovery was the most cost-intensive process after the fermentation.

Another important organic acid which is usually produced via fermentation is citric acid. It can be recovered by electrodialysis, similar to lactic acid. Moresi et al. published their results on the economic feasibility of citrate recovery by ED [196]. Here, the authors assumed a conventional citric acid production by *Aspergillus niger* which was fed with glucose or molasses. The broth was treated with calcium hydroxide to precipitate the citrate. After filtration and washing the precipitated calcium citrate was mixed with sulfuric acid to obtain the citric acid and calcium sulfate. This process was regarded as conventional which was then compared to a process concept with ED, where the citric acid was directly recovered from the fermentation broth. The ED operation was analyzed with respect to the investment costs and operating costs which were dependent on the plant capacity, current density and price of electric energy. The operating costs of ED were about 50% higher than that for the conventional process. Nevertheless, the authors preferred the new process with ED, because the disposal of large salt amounts could be avoided.

Novalic used a bipolar membrane stack to recover citric acid from sodium citrate [197]. Caustic soda was used to convert the salt into acid. A current efficiency of 69% and conversion efficiency of 96% was reached. Xu and Yang investigated the citric acid production via EDBM as well [198]. The authors fed sodium citrate solutions to the two compartment stack with one cation exchange membrane. During the operation the salt was split into citric acid and caustic soda. The electrode compartments were rinsed with sodium sulfate solution. The authors investigated the influence of the feed concentration and found that a concentration of 0.5–1.0 M sodium citrate solution allowed for the best efficiency.

Beside lactic and citric acid, further acids, such as L-malic acid [202], propionic acid [200], gluconic acid [199,203], L-ascorbic acid [201] and pyruvic acid [204] were produced or recovered by ED processes. A comprehensive summary of the investigated ED processes in the organic acid production is given in Table 3.

Table 3
Overview of investigated ED processes for organic acid production/ recovery.

Fermentation broth/model solution	Produced organic acid	Electrodialysis stack configuration	Ref.
Lactobacillus delbrueckii	Lactic acid	Conventional electrodialysis	[179]
Lactobacillus delbrueckii	Lactic acid	Conventional electrodialysis	[181]
Lactic acid bacteria	Lactic acid	Conventional electrodialysis	[186]
Lactococcus lactis	Lactic acid	Electrodialysis with bipolar membranes	[195]
Lactobacillus	Lactic acid	Electrodialysis with bipolar membranes	[183]
Lactobacillus	Lactic acid	Electrodialysis with bipolar membranes	[191]
Lactobacillus	Lactic acid	Conventional electrodialysis	[182]
Lactobacillus rhamnosus	Lactic acid	Conventional electrodialysis	[187]
Lactobacillus rhamnosus	Lactic acid	Conventional electrodialysis	[188]
Lactobacillus rhamnosus	Lactic acid	Conventional electrodialysis	[189]
Lactobacillus plantarum L 10	Lactic acid	Electrodialysis with bipolar membranes	[185]
Sodium lactate	Lactic acid	Conventional electrodialysis	[190]
Sodium lactate	Lactic acid	CED/ ISED	[180]
Sodium lacate	Lactic acid	Reverse electro-enhanced electrodialysis	[192]
Grass silage juice	Lactic acid	Conventional electrodialysis	[193]
Sodium citrate	Citric acid	Conventional electrodialysis	[196]
Lactococcus	Citric acid	Electrodialysis with bipolar membranes	[197]
Sodium citrate	Citric acid	Electrodialysis with bipolar membranes	[198]
Sodium glucanate	Gluconic acid	CED/ EDBM	[199]
Acidic propionic bacteria	Propionic acid	Electrodialysis with bipolar membranes	[200]
Sodium L-ascorbate	Ascorbic acid	Electrodialysis with bipolar membranes	[201]
Fumaric acid	L-malic acid	Conventional electrodialysis	[202]
Glucose Oxidase (GOD)	Gluconic acid	GOD immobilized on AEM	[203]
Sodium pyruvate	Pyruvate acid	CED/EDBM	[204]

4.2. Desalination

Shen et al. studied the desalination of glutamine product solution stemming from a fermentation broth via conventional electrodialysis (CED) [205]. The inorganic salts in the broth were represented by large amounts of ammonium sulfate (60 g L^{-1}) during the experiments. The starting concentration of the desired product glutamine was about 30 g L^{-1}. A good separation of the ammonium sulfate from glutamine could be achieved by controlling the pH at a value of 5.65 which was the isoelectric point of the product. Therefore, a removal of ammonium sulfate down to a value of about 2.4 g L^{-1} could be achieved with negligible losses of product of about 0.05%.

In a further publication, Shen et al. studied the desalination of a glutamic broth via conventional electrodialysis [206]. Here they found that a salt removal of 95 wt% could be achieved with a loss of product of about 20 wt%. The difference to the first publication with the representative substance system was explained by difficulties to control the pH during the ED operation, because OH^- ions present in the broth were also transported through the ion exchange membranes, resulting in a strong decrease of pH value.

Aghajanyan et al. performed conventional electrodialysis to desalt amino acid solutions stemming from cultured liquids in microbiological synthesis [207]. They investigated proline, valine and alanine fermentation permeates, containing inorganic ions such as NH_4^+, SO_4^{2-}, Na^+, K^+ or Cl^-. During ED operation the control of the pH value was essential to prevent the migration of proline (valine or alanine) ions through the membrane. To minimize the migration of H^+ ions from the feed solution into the concentrate and a subsequent decrease in pH value in the diluate (product solution), the ED stack was extended by a compartment surrounded by two anion exchange membranes. Hence, the loss of H^+ ions from the feed solution was significantly reduced, because they were trapped in this additional compartment. In result, the variance in pH value and the loss of proline from the product solution could be minimized.

A similar work was presented by Elisseeva et al. for the removal of sodium chloride and sucrose from synthetic amino acid glycine solutions via conventional electrodialysis [208]. The flux of amino acid through the ion-exchange membrane was highly dependent on the current density. Thus, the authors operated the ED process very close to the limiting current density. At such high current densities commencing water splitting caused a "barrier" effect regarding the transport of amino acid. The authors suggested performing a second run at lower, but still high current density to separate the glycine from sucrose. The glycine was attracted by the electric forces and transported through the membrane, while the sucrose was not affected by the electric field.

Rapp et al. studied the purification of spent black liquor from a Kraft process (see Section 3.5) by means of chloride removal via electrodialysis [209]. The chloride stemming from the processed raw materials accumulates while the liquor is recycled. Hence, it has to be removed continuously. The investigated liquor contained (besides the sodium hydroxide which is the Kraft liquor) potassium, sulfate, carbonate, bicarbonate and chloride. The electrodialysis set up comprised a stack of eight chambers with altering anion exchange and cation exchange membranes (conventional electrodialysis). The authors studied limiting current densities, membrane fouling and process economics with the result, that the system could be run about 90 h before fouling occurred with a limiting current density of about 10 mA cm^{-2} (for a chloride concentration of 0.5 g L^{-1}). The concentration of chloride could be reduced from 71 g L^{-1} to 4 g L^{-1}.

4.3. Fractionation of proteins and amino acids

An electrodialysis process for the isolation of amino acids was investigated by Readi et al. [210]. In this study, γ-aminobutyric acid (GABA) which is an enzymatic modification of glutamic acid, was separated from L-aspartic acid. GABA can be used in the food industry as well as in the production of industrial chemicals. First, the separation of glutamic acid and L-aspartic acid from other amino acids was investigated. This was possible, because these two amino acids exhibited very low isoelectric points (between pH 2.8 and 3.2) in comparison to other amino acids such as lysine or glycine (isoelectric points between pH 6 and 11). After separation of these two acids from the mixture, the authors suggested to convert the glutamic acid enzymatically to GABA in order to shift the isoelectric point of this compound. In result the isoelectric

points of the two remaining compounds differed in a broad range of pH 3–8 and could than be easily separated.

Bazinet et al. studied the fractionation of whey proteins which are of interest especially in the food industry with bipolar membrane electrodialysis [211]. Two different methods were investigated: (1) chemical acid (HCl) was added to the solution to shift the pH for enhancing the separation of the whey proteins, namely β-lactoglobulin, α-lactalbumin, immunoglobulin (Ig) and bovine serum albumin (BSA) and (2) acidification of whey protein solution was performed by application of BPMs to acidify the salts which were included in the feed solution. The second method was not just superior due to the elimination of chemicals, but also due to an enhanced protein recovery of up to 53% in comparison to 33% by the first method.

Ayala-Bribiesca et al. studied the occurrence of fouling during electrodialysis processing of whey protein diluate depending on the pH and mineral composition [212]. They found that under basic conditions the CEM was fouled by calcium which precipitated calcium hydroxide on the membrane surfaces and caused scaling. Under neutral or acidic conditions, the AEM was preferably fouled by proteins.

4.4. Electrophoretic fractionation of proteins

Originally, electrophoresis separates molecules only by charge and polarity differences. In so-called free-flow electrophoresis membranes are applied to protect the electrode compartments from the solution which shall be fractionated (see Fig. 20). Nevertheless, advanced applications extend the electrophoretic device with ultrafiltration membranes to allow for a separation due to two different physical mechanisms: (1) size exclusion and (2) differences in electrophoretic migration (see Fig. 21).

Several studies and developments have already been published on membrane assisted free flow electrophoresis over the past decades [214]. Aider et al. published a review on the applicability of electrophoresis (with and without membranes) in the bio-food industry [215]. They spotted four different possible fields: Protein separation, tobacco polyphenols separation, green tea catechins separation and simultaneous peptides separation. Referring to the topic of this current review paper the protein separation and the peptides separation seem to be the most interesting issues, as these compounds can be broadly utilized.

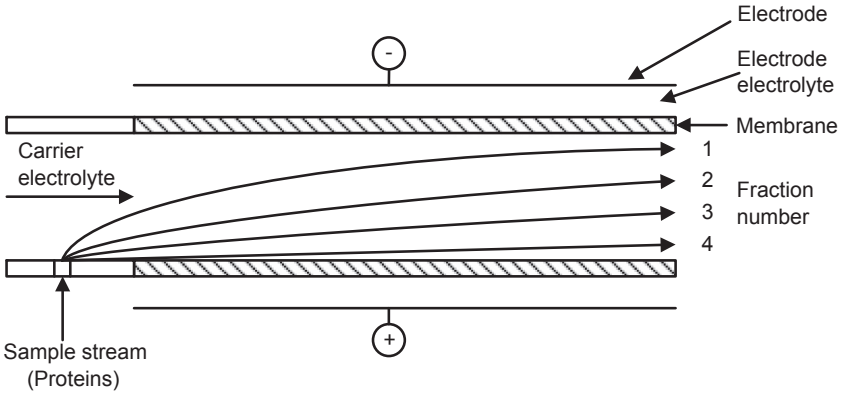

Fig. 20. Free-flow isoelectric electrophoresis [213].

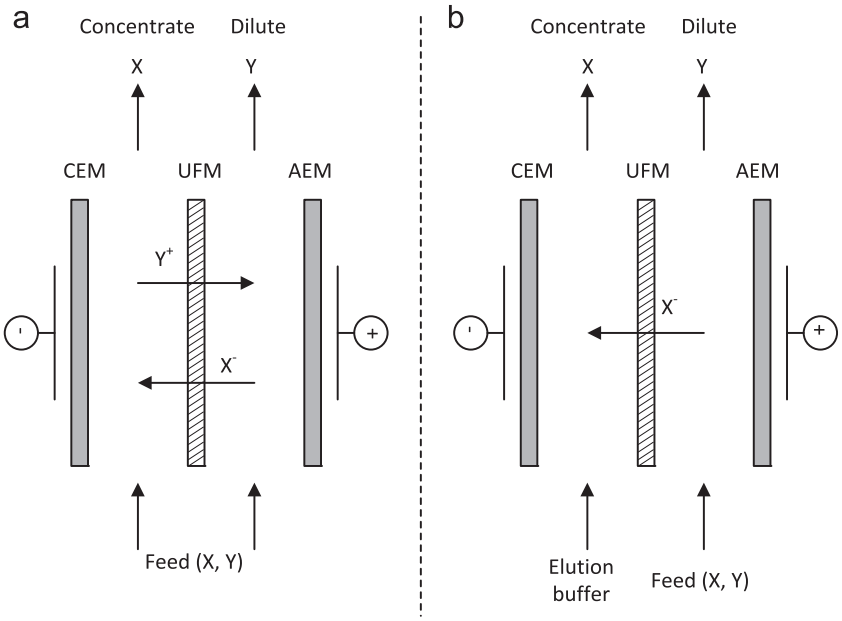

Fig. 21. Electrophoresis combined with ultrafiltration membrane (Gradiflow technique): (a) separation of protein *X* and *Y* and (b) concentration of protein *X* in one stream.

Poggel and Melin investigated the protein separation with a newly developed free flow electrophoresis apparatus. In this apparatus, the electrolyte compartments were shielded by ceramic membranes. The height of the separation channel was very narrow in order to provide constant thermal conditions. BSA and Cytochrome C proteins were chosen as model compounds to test the efficiency of the apparatus. Therefore, the channel height was reduced to a distance of 1 mm. A clean separation of the proteins could be reached at a pH of 4.3. Long term experiments verified the results. This work was extended to the application of a radial electrophoretic apparatus meant for application in technical scale [216].

Rylatt et al. used a set-up based on the patented *Gradiflow* technique (see Fig. 21) to separate proteins [217]. Ultrafiltration membranes are implemented into the feed channel of the electrophoresis to enhance the separation performance. In the cited publication, the authors used polyacrylamide membranes. They varied the applied voltage, the pH and buffer in order to discuss the basic phenomena which are decisive for an effective separation. The electro-migration of proteins such as BSA or Hemoglobin was studied depending on the pH. It could be shown, that due to different iso-electric points (the point at which a protein does not migrate within the electric field) a separation of the investigated proteins is possible. In addition, the migration of BSA through diverse ultrafiltration membranes installed in the apparatus was studied. For UF membranes with MWCO below 1000 kDa the transfer rate of BSA decreased.

Galier et al. also studied the separation of proteins, namely α-Lactalbumin and Bovine Hemoglobin in an electrophoretic membrane contactor [218]. Here the pH, the voltage and the type of membrane (anion exchange or cation exchange) was varied to validate theoretical calculations which were performed to determine the maximum possible product yield. Especially the inlet concentration influenced remarkably the productivity of the system.

Coleman and Mahler [219] used the gradiflow technique to separate two different monoclonal antibody fragments: (1) the fragment antigen-binding (Fab) and (2) the fragment crystallizable region (Fc) produced by papain digestion. Byproducts from the Fab preparation process were separated via size-exclusion with a polyacrylamide membrane. Simultaneously the two fragments Fab and Fc which were of similar size and could therefore not be separated with the ultrafiltration membrane, were separated according to their different charges. Therefore, a pH of 6.2 had to be adjusted with an accuracy of 0.5 pH units. At this pH the Fc was negatively charged and the Fab was positively charged. At this operating point the authors succeeded in separating the two fragments.

Bargeman et al. also combined the principle of electrophoresis with ultrafiltration to isolate bioactive peptides [220]. The set-up comprised two chambers which were separated by an ultrafiltration membrane. An anode was installed in the feed chamber, while the cathode was placed in the permeate chamber. During operation positively charged peptides moved from the feed solution into the permeate due to electrical driving forces, while neutral and negatively charged peptides remained in the feed solution. The separation of peptide α_{s2}-CN from a sodium caseinate solution was investigated with respect to the applied voltage of 40–60 V, the MWCO of the ultrafiltration membrane in a range between 25 and 100 kDa and the salt concentration of the feed solution. The transport of peptides increased linearly with the applied voltage. The authors suggested choosing a MWCO which is 3 fold bigger than the molecular weight of the peptide in order to avoid a strong reduction of the transport rate. The use of non-desalinated feed solution resulted in a decrease of the peptide transport rate, because further positively charged salts were concurrently transported to the permeate solution.

In summary, we conclude that electric-driven membrane processes allow for various separations such as organic acid recovery, desalination or even protein recovery. In organic acid recovery via electrodialysis research focuses on lactic acid almost exclusively. Different stack configurations were investigated such as the conventional electrodialysis or bipolar membrane electrodialysis. The examined processes have already been widely discussed in terms of mass transport issues, process integration and economy. Future research related to other biorefinery applications has to comprise investigations on the recovery of other acids beside lactic acid. Here, still a lack of fundamental understanding about the influence of recovered acid on the electrodialysis performance is present. Influencing parameters such as the molecular size of the acid, its solubility in the media/membrane, its acidity, kind of employed membrane, stack configuration, etc. have to be taken into account to allow for a predictable operation of an electrodialysis unit operation. Another question of interest will be the influence of residuals from a fermentation of lignocellulosic matter on the downstream electrodialysis separation such as furans or phenols.

Desalting in biorefinery applications via electrodialysis has not been addressed up to now. In future research this topic will become more relevant when large scale refineries with complete solvent recycling and utilization of the side-products will be set up. Then the relatively small amounts of salt from the fresh biomass will enrich in a process stream (the recovered pretreatment solvent for instance) and then lead to a relevant separation problem.

Furthermore, electrodialysis and electrophoresis with and w/o membrane technique allow for the separation of highly valuable proteins. To evaluate the membrane unit operations in terms of productivity and economy they have to be compared with the respective established techniques such as chromatography. Little is known with respect to these challenges.

5. Prospective membrane processes

In this section membrane processes in biorefinery applications are discussed which have yet not reached technical or even industrial scale, but are prospective. First candidate for interesting new research with integrated membrane technology is the solid state fermentation process (S-SF). For S-SF, a biofilm is cultivated on a flat solid underground which allows for a simultaneous saccharification and fermentation (SSF) of biomass to biofuel. Due to the high density of substrates, enzymes and microbes in the biofilm the productivity is considerably increased in comparison to the conventional process design of separated saccharification and fermentation of (cellulosic) biomass. For example, biofilms consisting of *Clostridium thermocellum* allowed for 2.7–4.7 fold higher rates of specific hydrolysis than cell-free cellulase from the same organism. This phenomenon was contributed to enzyme-microbe synergy effects in the biofilm [221].

Thus, SSF systems are presumed to be effective especially in the processing of lignocellulosic material. Here, conventional fermentation systems suffer from low reaction speeds and low conversion rates. Biofilms may enhance the conversion kinetics by allowing several specialized enzymes to interact in a probably multilayered dense packed environment. The density of microbial structure may even lead to the interactive accumulation of species which otherwise do not evolve [222]. The success of such systems is highly dependent on the backlayer on which the biofilm grows. The backlayer has to allow biological matter to attach onto its surface (biocompatibility, surface charge, sterilization). On the other hand, the occurrence of fouling in terms of change of membrane material during time or growth of film into the material has to

be avoided. The backlayer has to provide some kind of permeability for oxygen which has to be supplied to the biofilm. A membrane would allow for the growth of biofilm on the front side and for supply of fresh oxygen through the back side. As well the membrane could enhance the removal of rate-limiting CO or CO_2 gas from the biofilm. A process scheme is shown in Fig. 22.

Matsumoto et al. studied the possibility to utilize such a membrane-aerated biofilm for simultaneous nitrification and denitrification of wastewater via model simulations [223]. They concluded that for biofilms with a thickness from 600 to 1200 μm, a high nitrogen removal efficiency of more than 70% could be achieved for carbon/nitrogen ratios from 3.0 to 5.25. Wang et al. even proposed the application of membrane biofilms in biofuel production [222]. They envisioned a highly consolidated bioprocess (HCBP) which incorporates delignification, saccharification, co-fermentation and separation in a single reactor inhabited by a multispecies biofilm.

A prospective membrane device is the membrane reactor which allows for enhanced conversion rates in the production of biomolecules [224,225]. Here, membranes as (catalytic) adsorbent materials are applied in order to replace packed bed reactors, especially in the refinery of biomolecules. Biochemical conversions usually take place at moderate temperatures. Due to the mild process conditions the low thermal stability of applied membranes does not limit the applicability of membrane reactors. Furthermore, conventional chemical catalysts are often inactive below high temperatures what is one more advantage for the membrane reactor. For development of sustainable production routes, the application of this technique can help to reduce the energy consumption directly in upstream processing.

In the publication of Guerreiro, membranes such as the Nafion were selected to serve as solid acid catalysts [224]. These membranes were placed in a membrane reactor (see Fig. 23). The membranes encouraged the convertion of waste fats or non-edible type oils to methyl esters which is similar to the transesterfication of soybean oil (see Section 3.1). The efficiency of the membrane reactor was than compared with the efficiency of solid catalysts in the shape of pellets. Experimental results showed that glycerol was enriched in the solid pellets leading to a rapid decrease in conversion rates. In the membrane reactor the undesired deposition of glycerol could be avoided. Shi et al. investigated the applicability of a membrane reactor for enhanced biodiesel production as well [226]. They obtained conversion rates of free fatty acid to methyl esters of up to 94.5% for a catalytic membrane consisting of $Zr(SO_4)_2$ and sulfonated PVA.

A membrane reactor was also compared to the conventional packed bed reactor in the purification of proteins from plant extractants. In the publication of Menkhaus et al. the authors discussed the recovery of native proteins stemming from corn or soybean as side-products within biorefinery processes [227]. Membrane adsorption provided a faster throughput and greater binding of native proteins for a given volume of adsorption medium. Hence, a more efficient recovery of native protein side-products and highly purified recombinant products was achieved in comparison with the packed bed reactor. For this application, several membranes have already been investigated or prepared. Examples are hybrid catalytic membranes consisting of cation ion-exchange resin particles and polyethersulfone [228], organic–inorganic hybrid membranes prepared from zirconium sulfate and sulfonated poly(vinyl alcohol) [226], polystyrene sulfonic acid/polyvinylalcohol (PSSA/PVA) membranes [229], polymer membranes containing sulfonic acid groups [230] or sodium polyethylene-5-sulfoisophthalate/polyethylene sulfonate (SPES/PES) catalytic membranes [231].

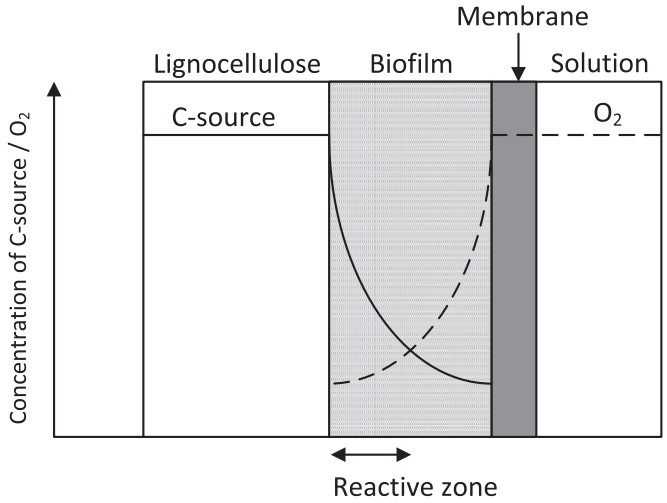

Fig. 22. Membrane as support of the biofilm in a solid state fermentation process [222].

6. Conclusion and outlook

This review illustrates recent developments in biorefinery systems with the focus on membrane separations. The most frequently investigated processes of ultrafiltration and pervaporation of bioethanol from fermentation broth were discussed, because they are both 1st generation biofuel processes. In the production of bioethanol sugar cane or pretreated corn is fermented, yielding low concentrated alcohol solutions which are recovered from the broth by pervaporation membranes. Here, the most interesting issue for the operation of a bio-reactor with integrated ultrafiltration membranes is to avoid fouling on the membrane surface in order to allow constant high permeate fluxes during continuous operation of the system. In recent publications membrane bioreactors were run continuously for up to 400 h.

In downstream processing of the recovered water/ethanol mixture, pervaporation membranes are applied to concentrate ethanol in aqueous solution (hydrophobic PV) and to dewater highly concentrated ethanol (hydrophilic PV). For this purpose several membrane materials, such as zeolites, ceramics, polymers or mixed-matrix membranes were produced and tested for there

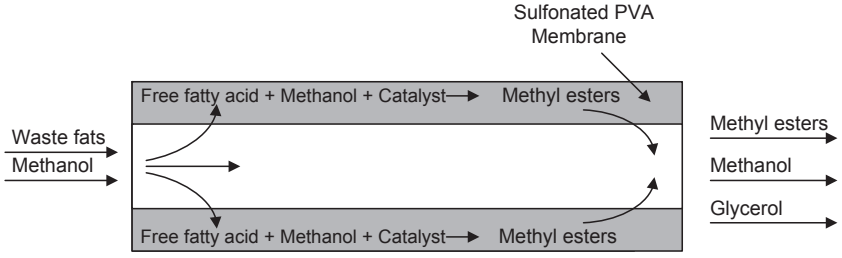

Fig. 23. Membrane reactor for the production of methyl esters from waste fats or non-edible type oils [224].

applicability in water/ethanol separation with the requirements of providing high separation factors and high permeate fluxes at low production costs for the membrane. Typically zeolite membranes provide very high separation factors, but suffer from high production costs. Polymeric membranes, e.g. polyimide membranes are inexpensive in production, but offer only mediocre separation factors. Another important issue is the integration of pervaporation membranes in bioethanol production processes which already operate with thermal devices such as distillation or stripping columns. Here, the implementation of pervaporation can efficiently reduce the energy demand of the column, when the condenser at the top can be replaced by the membrane module. In order to enhance the yield of fermentation-based ethanol-production processes, ultrafiltration membranes were implemented in downstream processing of the stillage, formerly leaving the fermentation process as waste stream. Here, valuable side-products were recovered such as nutrients or proteins which can then be fed back to the fermentor or bioreactor.

In the direct conversion of sugar cane to white sugar, ultrafiltration membranes were applied to purify sugar cane juice before final crystallization. Prior to this process variant, sulfur dioxide was added to the sugar cane juice to remove colorants or other impurities by coagulation and precipitation. But the addition of sulfur dioxide resulted in an inefficient removal of undesired compounds and additional sulfite in the final product white sugar. The product quality could be enhanced by replacing the sulfitation step with an ultrafiltration process.

In the production of 1st generation biodiesel — a highly purified methyl ester — from canola oil, the application of an ultrafiltration membrane reactor was very well studied in several publications. In the membrane reactor, the canola oil – triglyceride – was dispersed in methanol which acted as catalyst and feed solution. The triglyceride formed μm-size droplets. The dispersion flew inside a tubular membrane module, where the triglyceride was consecutively converted to diglyceride and monoglyceride, releasing at any one time methyl ester. The methyl ester was soluble in the ethanol solution and could pass the membrane, while the glyceride droplets were rejected by the membrane. The continuous removal of methyl ester from the dispersion shifted the reaction equilibrium to the product side. For this process already experiments were reported which were run over 10 months without any notable loss in performance of the membrane.

In biorefineries utilizing lignocellulosic matter as raw material, the most established process is (1) the Kraft process and (2) the Organosolv process. In the Kraft process which was originally intended to obtain cellulose for the paper production, ultrafiltration and nanofiltration membrane processes were implemented to recover lignin from the spent liquor. In the Organosolv process, where the lignocellulosic biomass is pretreated with water/ethanol mixtures, ultrafiltration membranes are utilized as well to recover undissolved lignin from the solvent. Another issue in these processes was the recovery of spent solvent. Electrodialysis was successfully applied to remove residues such as salt from the solvent.

For the recovery of amino acids or carbonic acids stemming from bio-macromolecular matter, the most promising technique is electrodialysis. It is applied for the separation of lactic acid from a fermentation broth or a grass silage stream. If the lactic acid is produced via fermentation, it is typically obtained as sodium lactate salt. In a conventional electrodialysis process, using alternating cation exchange membranes and anion exchange membranes, the sodium lactate is separated from uncharged compounds in the fermentation broth and is simultaneously concentrated. In a second electrodialysis process, bipolar membranes are applied to split the salt into the respective acid – here lactate acid – and the base – here caustic soda. For the first electrodialysis process of sodium lactate separation from the broth, a process variant was developed, in which the feed stream was led directly through the electrode chambers. This process scheme offers two advantages: (1) a minimum membrane configuration is provided and (2) fouling of the membranes is avoided by alternating the current periodically. Therefore, this set-up is predestinated for in situ recovery of lactic acid from the fermentation broth.

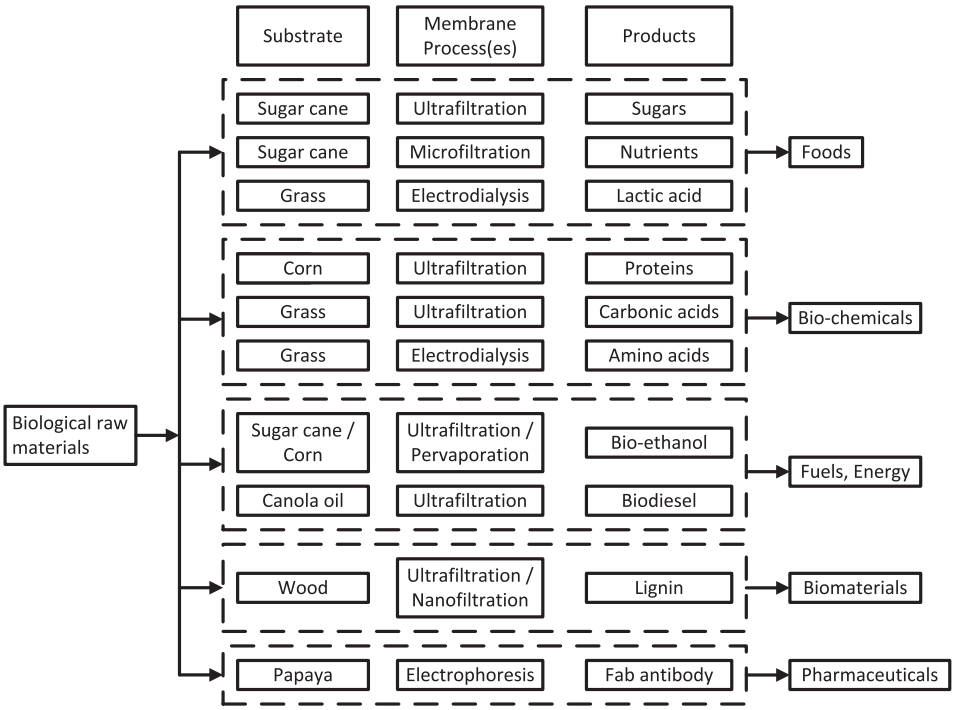

Fig. 24. Visualization of already described biorefinery processes with integrated membrane operation units.

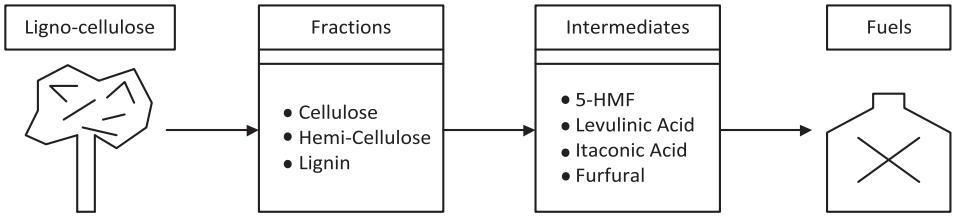

Fig. 25. Simplified process concept of the excellence cluster Tailor-Made Fuels from Biomass (TMFB) at the RWTH Aachen University.

Other electrical driven membrane processes deal with the separation of amino acids via electrodialysis or separation of proteins via electrophoresis coupled with ultrafiltration (Gradiflow technique). Here the control of the pH value is very important in order to separate very similar components due to their differences in the iso-electric point at which the net charge of a compound is zero. For example, in the fractionation of two different monoclonal antibody fragments with the Gradiflow electrophoresis technique, the pH value had to be adjusted with an accuracy of 0.5 pH units.

Fig. 24 concludes the most important process routes addressed in this review. In comparison to Fig. 1 it becomes obvious that many biorefinery downstream processes can be realized with membrane technique. As an outlook, we will describe the complexity of designing a biorefinery downstream process through examples related to a next generation biorefinery.

The process is currently conceptually developed at the RWTH Aachen University within the DFG-Excellence Cluster 'Tailor-Made Fuels from Biomass'. The biorefinery addresses the efficient conversion of lignocellulosic materials to fuel compounds. In particular, the conversion of biomass based on low-temperature solvent pretreatment and direct (bio-) chemical conversion to the respective target molecules is investigated in order to avoid high temperature levels and energy consumption of gasification with consecutive built up of macromolecules via Fischer–Tropsch synthesis [232].

Research includes the development and optimization of novel solvent systems allowing for a low energy-consuming dissolution of biomass, respectively cellulose [233]. The influence of the solvent system – in this case ionic liquids – on the downstream enzymatic hydrolysis of cellulose to glucose monomers is part of the investigations as well [234]. Within the cluster the conversion of glucose to the platform chemical itaconic acid by fermentation with the fungus *Ustilago maydis* [235,236] and chemical conversion to promising fuel candidates such as 2-Methyltetrahydrofuran (2-MTHF) is pursued [237]. The efficiency of the investigated processes is examined as well and evaluated in detail in order to realistically assess chances and risks of proposed process concepts [238]. To complement the research by means of establishing a 'complete' biorefinery, the utilization of cellulosic matter to other products beside fuels has already been revised [239].

In Fig. 25 the basic concept of the TMFB biorefinery is schematically drawn. The focus is set on the conversion of lignocellulosic biomass which can be grass or wood, to biofuel. After more or less intensive pretreatment of the biomass, its most important fractions, namely cellulose and hemicellulose are processed to the intermediates 5-HMF, levulinic acid, itaconic acid and furfural. These intermediates offer the opportunity of a high flexibility in terms of possible final products. Even though the production of a biofuel is the key issue of the cluster, the implementation of this intermediary level preserves the chance to follow interesting side-processes for the production of e.g. furans, esters or aromatic compounds, what follows the idea of a biorefinery.

In this frame of interdisciplinary research, membrane technology plays an important role for process engineering. One pathway followed within the cluster is the biomass pretreatment with ionic liquids. Here it could be shown, that nanofiltration membranes are capable to separate the solvent from lignocellulosic substrates and to recover valuable products such as glucose [240]. In downstream processing of the glucose fermentation to itaconic acid, the recovery of valuable substances from the fermentation broth is carried out via in situ ultrafiltration. Here an extensive review was published to point out the opportunities of in situ product recovery from a fermentation broth [132]. In addition a novel micro-/ultrafiltration process for in situ product removal from a fermentation broth principally based on the flow reversal technique shown in Fig. 13b was developed [241]. As opposed to the usual operation mode, the flow reversal has not just the function to dispense filter cake from the membrane surface, but also to introduce fresh nutrient solution into the fermentor. Product solution is continuously replaced by nutrient solution allowing for a very stable operation of the membrane bioreactor system compared to a conventional system, where the nutrient is fed intermittently. In addition, cake layer formation is avoided, since no net flux over the membrane occurs. Hence, this process is coined flow reversal diafiltration. The separation, concentration and purification of the product solution – in this case itaconic acid – from the broth is also investigated by means of bipolar membrane electrodialysis. Here it could be proven, that the production of membranes with very low leakage rates is possible and that their implementation into an acidification process is promising [242].

If biorefineries become industrial reality in the near future, the following opportunities and challenges exist for membrane separation processes:

- Above all, the biorefinery process needs to strive for a Zero Discharge Process: all components of the biomass need to find a valuable destination [243]. Useful lignin applications will be the largest challenge.
- Recovery/purification of solvents after pretreatment of biomass via ultra-respectively nanofiltration are important. Complete solvent recovery contributes to the Zero Liquid Discharge Biorefinery in the future. A cascaded fractionation of the particulates/solutes is of utmost importance in order to utilize side-products, such as hemi-cellulose or lignin.
- Recovery/purification of solvents and ashes/salts stemming from the biomass need to be utilized as well. Here, nanofiltration or electrodialysis are favored processes.
- Design and simulation of complete process routes will enable a realistic judgment of the feasibility of membrane supported biorefinery concepts.
- Knowledge on impurities is required to understand carry over effects of impurities between separation and conversion operations. For membrane processes, these impurities may complicate the fouling behavior with realistic feed solutions.
- Such impurities may also require adaption and optimization of membrane processes to allow long-term stable operation.

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